The action of the sulfides of the alkali and alkaline earth metals in these amines is interesting. Samples of the commercial variety of these salts when treated with the amines give yellow solutions very similar to a dilute solution of sulfur. The residual salts, which previously were a dirty yellow in color, are reduced to a pure white color and a granular condition. It is suggested that any free sulfur present in the sulfides is dissolved and the polysulfides thus reduced to the normal sulfides. This explanation, if correct, indicates a possible method of purifying these compounds.

Summary.

The results of this study show that the simpler primary and secondary amines at room temperatures are fair solvents for many salts. However, the solubilities have high temperature coefficients and at the boiling-point of liquid ammonia but very few salts are perceptibly soluble in any of the amines.

The work outlined in this paper was done at the suggestion and under the direction of Professor E. C. Franklin, and I wish to thank him for his kind advice and assistance.

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ORGANIC MOLECULAR COMPOUNDS. II.

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It was shown some time ago[1] that tetraphenyl-ethylene dichloride, $(C_6H_5)_2CCl.ClC(C_6H_5)_2$, forms well characterized molecular compounds with chloroform and carbon tetrachloride. The existence of these addition-products led to a study of substances of similar and related structures, and it was discovered that organic compounds of certain types possess to a high degree the power to form molecular compounds.[2] Among the substances studied were substitution-products of tetraphenyl-ethylene. Of these *p*-tetrabromo-tetraphenyl-ethylene, $(BrC_6H_4)_2C = C(C_6H_4Br)_2$, was noteworthy as it formed well crystallized compounds with acetone, methylethyl ketone, ether, carbon tetrachloride, ethyl acetate, and benzene.

As a result of an attempt to interpret the facts discovered and the endeavor to guide future work an hypothesis was devised. A large number of molecular compounds, both inorganic and organic, have been described, but no adequate explanation of their structure based on our present views of valence has been proposed. The subject is an important one, and it

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[1] Norris, Thomas and Brown, *Ber.*, **43**, 2940 (1910).

[2] Norris, THIS JOURNAL, **38**, 702 (1916).

seemed advisable to study it further, especially in the field of organic chemistry, since the chemist has it in his power to change gradually by the use of the proper substituents the nature of the molecule and thus develop or reduce its ability to form addition-products with other substances. In this way by knowing the effect of the substituents introduced on the general properties of the molecule and on its ability to form molecular compounds, relationships might be traced and the factors underlying the addition discovered.

The hypothesis which has served as a guide in a study of these compounds is as follows.

1. The molecular compound is formed as a result of the coming into play of latent affinities residing on an atom in each of the constituents of the compound. For example, the molecular compound of triphenylchloromethane and acetone, $[(C_6H_5)_3C.Cl]_2.(CH_3)_2CO$, is produced as a result of the fact that the chlorine atoms of the methane derivative and the oxygen atoms of the ketone possess latent affinities of such activity that they interact and a molecular compound results.

2. All atoms possess these latent affinities. Whether or not they are of such a nature as to permit the union of a molecule with a second molecule is determined by the extent to which the chemical energy of the atom in question has been expended when the molecule containing it was formed. If an atom in a compound reacts with difficulty when the latter is brought into contact with other substances it is evident that a large part of its energy has been expended and but a little of it remains to take part in reaction. On the other hand, if the atom enters into reaction readily with other substances it is evident that it still possesses available energy. It is probable, therefore, that such active atoms might be able to unite with atoms of a similar nature and form molecular compounds. For example, the chlorine in methyl chloride is firmly bound in the molecule; it does not form stable molecular compounds. Triphenyl-methyl chloride contains a chlorine atom that is very active; the compound is readily hydrolyzed, and reacts in the cold with sulfuric acid, and with silver. The active chlorine, according to the hypothesis put forward here, contains sufficient energy to form molecular compounds with other substances containing active elements. A study of the literature confirms the view that compounds containing unusually active elements or groups form well characterized molecular compounds.

3. Substances which contain inactive double bonds form molecular compounds. In most cases direct addition of atoms or groups at the double bond leads to the formation of ordinary saturated compounds. So-called unsaturated compounds, however, are known in which the unsaturation is so slight that they will not unite with such an active element as bromine. The chemical affinity latent in the double bond is

so small that it cannot hold in combination other atoms or groups linked to it by primary valence bonds. Many such compounds, however, form well-characterized molecular compounds. The available energy of the double bond is not enough to neutralize the energy of atoms and form a true valence bond, but is sufficient to interact with a similar small amount of energy residing in another compound. Many cases of this type have been discovered. For example, *p*-tetrabromo-tetraphenyl-ethylene contains a very inactive double bond; it will not add bromine; but it forms a large number of molecular compounds with a great variety of substances.

With the hypothesis stated above as a guide a number of compounds have been investigated and a variety of new molecular compounds discovered.

It is impossible to test the proposed hypothesis rigidly, as we have at present no quantitative measure of the relative activities of halogen atoms in organic compounds or of the unsaturation of a double bond. The results of the work described below were obtained in connection with a research on the factors which influence the activity of halogen atoms joined to carbon.[1] When a quantitative measure of this activity has been arrived at by the methods now being developed it is hoped that an interpretation of the facts described below will be possible. As the authors are unable to collaborate in the work in the future, it seems advisable to publish the results so far obtained.

The following molecular compounds have been reported in papers already published.

1. From compounds containing active atoms or groups: (*a*) compounds containing tetraphenyl-ethylene dichloride, $(C_6H_5)_2CCl.ClC(C_6H_5)_2$, (M), of the following composition: $M.2CHCl_3$, $M.2CCl_4$, $M.2CHBr_3$, $M.2CBr_4$, $M.2CHBrCl_2$, $M.2SO_2Cl_2$; (*b*) compounds containing *p*-chloro-tetraphenyl-ethylene dichloride, $ClC_6H_4.C_6H_5CCl.ClC(C_6H_5)_2$, (M′): $M'.CHCl_3$, $M'2CCl_4$; (*c*) compounds containing triphenyl-chloromethane, $(C_6H_5)_3C.$-Cl, (M″): $4M''.3CCl_4$:[4] $2M''.(CH_3)_2CO$; (*d*) compounds containing triphenyl-carbinol, $(C_6H_5)_3COH$, (M‴): $4M'''.3CCl_4$, $2M'''.(CH_3)_2CO$.

2. Addition-products from compounds containing an inactive double bond, *p*-tetrabromo-tetraphenyl-ethylene, $(BrC_6H_4)_2C = C(C_6H_4Br)_2$, (N): $N.2(CH_3)_2CO$, $N.CH_3COC_2H_5$, $N.(C_2H_5)_2CO$, $N.CCl_4$, $N.CH_3COOC_2H_5$, $N.C_6H_6$.

On account of the unusual ability of tetrabromo-tetraphenyl-ethylene to form molecular compounds the substance has been investigated fur-

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[1] This work of which this paper is a minor part was aided by a grant from the Warren Fund of the American Academy of Arts and Sciences.

[2] The formula for this compound given in the previous paper is incorrect. The analytical results are correctly given, but these correspond more closely to the above formula than to the one given.

ther to determine whether molecules belonging to other classes of compounds than those studied would enter into combination with it, and to discover the effect of the molecular weight of the added compound on the stability of the addition-products. Well-crystallized molecular compounds were obtained containing in each case one molecule of the ethylene derivative and one molecule of one of the following, toluene, *p*-xylene, chlorobenzene, ethyl ether, propyl acetate, ethyl propionate, and ethyl acetate. No compounds were isolated at ordinary temperatures with chloroform, ethyl alcohol, amyl alcohol, bromobenzene, *m*-xylene, iodobenzene, petroleum ether, methyl acetate, or ethyl formate. It was found that the fact that the ethylene derivative formed no compound with alcohol and with *m*-xylene could be used to separate acetone from alcohol and *p*-xylene from *m*-xylene.

In order to determine the effect of the replacement of bromine by chlorine, tetrachloro-tetraphenyl-ethylene was next studied. In this case the ability to form molecular compounds was much reduced. Of the compounds studied addition-products were obtained only with benzene, carbon tetrachloride, and methylethyl ketone.

Monochloro-tetraphenyl-ethylene was next studied. In this case a compound with carbon tetrachloride only was formed. Negative results were obtained with the substances that yielded well-characterized addition-products with the bromine substitution product. Tetraphenyl-ethylene yielded no molecular compounds. It is impossible to say at present whether the falling off in the ability to form molecular compounds is associated with change in molecular weight or the change in the inactivity of the double bond which is associated with the change resulting from the alteration of the substituents. It is improbable that the formation of the molecular compounds can be attributed directly to the halogen atoms in the tetraphenyl-ethylene derivatives, on account of the fact that in the compounds studied in which the formation of double molecules can be traced to the halogen atoms present, chlorine is more efficient in this respect than bromine. Triphenyl-chloromethane, for example, forms molecular compounds, whereas analogues with triphenyl-bromomethane do not exist.

Since molecular compounds had been formed from triphenyl-chloromethane and triphenyl-carbinol it appeared of interest to investigate diphenyl-chloromethane and diphenyl-carbinol. No molecular compounds were isolated. To determine whether increase in molecular weight produced any effect *p*-phenyl-diphenyl carbinol was studied; it yielded a compound with carbon tetrachloride which contained one molecule each of its constituents. *p*-Phenyl-diphenyl-chloromethane formed a molecular compound with carbon tetrachloride containing two molecules of the former to one of the latter. No molecular compound was formed from *p*-bromo-diphenyl-carbinol and carbon tetrachloride nor from *p,p'*-dichloro-diphenyl-carbinol.

A study of the literature is being made with the hope that generalizations of value may be arrived at. Up to the present a large number of compounds have been tabulated.

Experimental Part.

Experiments with *p*-Tetrabromo-tetraphenyl-ethylene.—The substance was prepared from tetraphenyl-ethylene as follows. Five g. of the finely ground hydrocarbon was spread in a thin layer on the bottom of a beaker and treated with 7.5 cc. of bromine. The mixture was allowed to stand overnight and the colorless product crystallized from hot xylene in which it is readily soluble. On cooling the bromine derivative separates in large, well-formed crystals.

Preparation of the Compound *p*-$(BrC_6H_4)_2C = C(C_6H_4Br)_2.C_6H_5CH_3$.—The bromine derivative was dissolved in boiling toluene, free from benzene. On cooling, radiating, shiny, transparent needles separated, which slowly became opaque on standing. A sample was dried for 10 minutes on a porous plate, weighed, and heated to constant weight at 110°. The loss in weight calculated for the above formula is 12.44% the loss found was 12.29%.

Preparation of the Compound *p*-$(BrC_6H_6)_2C = C(C_6H_4Br)_2.C_6H_5Cl$.—This compound was formed by crystallizing the bromine derivative from boiling chlorobenzene. It slowly effloresced in the air. The theoretical loss in weight is 14.79%. The loss found depended on the time the crystals stood in the air before being weighed. The percentages obtained were 13.81 and 15.41.

Preparation of the Compound *p*-$(BrC_6H_4)_2C = C(C_6H_4Br)_2.(C_6H_5)_2O$.—When tetrabromo-tetraphenyl-ethylene was dissolved in boiling ether, in which it is difficultly soluble, and the solution evaporated so that the product separated while the latter was hot, well-defined crystals of the ethylene derivative free from ether were formed. When a cold saturated solution was allowed to evaporate spontaneously at room temperature two kinds of crystals were obtained, transparent and opaque. Neither kind lost weight when heated. When a dilute solution at about —10° was evaporated slowly in a stream of air, shiny, transparent crystals were obtained which became opaque on standing in the air. Some of these crystals after standing on a porous plate for 5 minutes were weighed and heated at 110° The loss in weight was 9.38%; the theoretical loss for a compound of the above formula is 10.25%.

Preparation of the Compound *p*-$(BrC_6H_4)_2C = C(C_6H_4Br)_2$.*p*-$C_6H_4(CH_3)_2$.—The xylene used boiled at 136° to 138° and solidified in ice-water. The compound was obtained when a hot saturated solution cooled to room temperature. It effloresced very slowly in the air. The crystals were weighed 15 minutes after removal from solution; the weight remained constant for 30 minutes, and then the crystals were heated to 110°. The weight lost was 14.85%, while the theoretical loss is 14.06%.

Attempts were made to prepare a molecular compound with *m*-xylene. Crystals were obtained by rapid and slow evaporation, but no compound was formed.

Tetrabromo-tetraphenyl-ethylene was crystallized from commercial xylene. The crystals obtained from a hot solution did not lose weight on heating. Those obtained by spontaneous evaporation lost 11.93% on heating. It is probable that the xylene present in the molecular compound which united with the bromine derivative was *p*-xylene. The *ortho* compound was not available for experimentation.

Preparation of the Compounds $(BrC_6H_4)_2C = C(C_6H_4Br)_2.CH_3COC_3H_7$, $(BrC_6H_4)_2C = C(C_6H_4Br)_2.C_2H_5COOC_2H_5$, $(BrC_6H_4)_2C = C(C_6H_4Br)_2.CH_3COOC_3H_7$.—These compounds were obtained by dissolving the ethylene derivative in the boiling liquids. In the 3 cases transparent crystals which effloresced rapidly in the air separated on cooling. The actual and theoretical losses were, respectively, 11.93 and 11.71, 13.54 and 13.60, and 12.15 and 13.60%.

Attempts to Prepare Molecular Compounds with Other Substances.—No compounds with tetrabromo-tetraphenyl-ethylene were formed at room temperature with ethyl alcohol, *iso*-amyl alcohol, bromobenzene, iodobenzene, petroleum ether. Experiments in which solutions of the ethylene derivative in methyl acetate, ethyl formate, and chloroform were evaporated at —25° yielded no molecular compounds.

Experiments with a Mixture Containing Acetone and Ethyl Alcohol.—Tetrabromo-tetraphenyl-ethylene forms a compound with acetone but not with ethyl alcohol. It seemed of interest to determine what proportion of acetone must be present in the mixture of the ketone and the alcohol to permit the formation of a compound with the former. A study of various mixtures led to the conclusion that a relatively small amount of the alcohol prevented the molecular compound from being formed. When 6 volumes of the ketone and one of the alcohol were present the molecular compound was formed; when 5 volumes was used a mixture of crystals was obtained; and with 4 of the ketone and one of the alcohol no molecular compound separated.

Experiments with a Mixture Containing Acetone and Chloroform.—Tetrabromo-tetraphenyl-ethylene does not form a compound with chloroform. When the former was dissolved in a mixture of 9 volumes of acetone and one volume of chloroform, crystals of the molecular compound with acetone were obtained. These were dried in the air and then gently heated and the acetone given off collected. This was found to be free from halogen compounds. This and the experiment described above indicate that these molecular compounds could be used to prepare pure solvents.

Experiments with *p*-Tetrachloro-tetraphenyl-ethylene, $(ClC_6H_4)_2C = C(C_6H_4Cl)_2$.[1] The ethylene derivative was prepared by a new method which appears to be more satisfactory than the one described. *p-p'*-Dichloro-diphenyl-carbinol was first prepared from the corresponding ketone. Twenty g. of the latter, 20 g. of zinc dust, 12 g. of sodium hydroxide, and 300 cc. of alcohol were boiled for 3 hours and filtered hot. To the solution water was added, when the carbinol was precipitated. This was crystallized from 60 cc. of alcohol, and then melted at 91.5°. The yield was nearly that theoretically possible.

Eight g. of *p-p'*-dichloro-phenyl-carbinol was heated to the boiling-point with 10 cc. of the constant-boiling mixture of water and hydrobromic acid for 3 hours. The product, dichloro-diphenyl-bromomethane, was extracted with carbon disulfide. On evaporation of the solvent it wa taken up in ether, from which it was obtained in crystals which melted at 70–71°. These were heated in a flask in an oil-bath at 150° for 3 hours, and finally cautiously with a small free flame as long as hydrogen bromide was given off. The contents of the flask were then dissolved in boiling carbon tetrachloride in which the compound·is difficultly soluble. On cooling a molecular compound of tetrachloro-tetraphenyl-ethylene separated which lost carbon tetrachloride on standing.

Preparation of the Compound $(ClC_6H_4)_2C = C(C_6H_4Cl)_2.2CCl_4$.—This compound was obtained by allowing the ethylene derivative to crystallize from carbon tetrachloride at room temperature. It loses the added chloride very slowly. The percentage loss found was 39.66: the calculated loss is 39.59%.

Preparation of the Compound $(ClC_6H_4)_6C = C(C_6H_4Cl)_2.2CH_3COCH_3$.—At room temperature a molecular compound is not formed. When the solution is evaporated at the temperature of a bath of calcium chloride and ice well-formed crystals of the molecular compound separated. Calculated loss for the above formula, 19.80%; that found was 21.6%. The compound effloresced very rapidly at room temperature, and lost 20% of its weight in 40 minutes.

Preparation of the Compounds $(ClC_6H_4)_2C = C(C_6H_4Cl)_6.C_6H_6$ and $(ClC_6H_4)_2C = C(C_6H_4Cl)_2.CH_3COC_2H_5$.—These compounds were obtained when hot solutions cooled to room temperature. The calculated and obtained losses on heating to 110° were, respectively, 14.23 and 15.35% and 13.28 and 13.58%. No compound was obtained with ethyl acetate.

Experiments with *p*-Chloro-tetraphenyl-ethylene, $ClC_6H_4.C_6H_5C = C(C_6H_5)_2$.—This compound was prepared by an improved method; 15 g. of *p*-chloro-benzophenone chloride and 9 g. of diphenyl-methane were

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[1] The work on this compound was done by Paul G. Woodward.

heated together in an oil-bath for 2 hours at 170°. The temperature was slowly raised during 3.5 hours to 225° at which temperature the heating was continued for 2 hours. The mixture was then heated with a small flame for 2 hours more. On standing overnight the product changed to a mass of crystals, which, after washing with water, were recrystallized from alcohol. The compound melted at 162°; the yield was 15 g.

The monochloro derivative of tetraphenyl-ethylene did not form a compound with carbon tetrachloride at room temperature, but when a solution of the compound in carbon tetrachloride was evaporated at —15° small crystals were obtained which effloresced rapidly at room temperature. The crystals were removed from the solvent and placed on a porous plate, which had been previously cooled in a desiccator. After standing for 3 minutes the crystals were weighed and heated. The loss in weight calculated for a compound of the formula $ClC_6H_4.C_6H_5C = C(C_6H_5)_2.2CCl_4$ is 45.69%; that found was 47.10%. When the molecular compound was kept at room temperature for 15 minutes before the determination in loss of weight was made the value found was 38.90%. There was evident decomposition of the compound. No molecular compounds could be isolated with benzene, methylpropyl ketone, or acetone.

Preparation of the Compound $C_6H_5C_6H_4.C_6H_5CHOH.CCl_4$.—No compound was formed at room temperature but at —10° crystals separated from the solvent that corresponded in composition to the above formula. The loss in weight obtained was 37.47%; that calculated was 37.19%. It is of interest to note in this connection that no molecular compound of diphenyl-carbinol and carbon tetrachloride could be isolated at —20°. This fact is in accord with the general conclusion that increase in molecular weight favors the formation of such compounds.

No addition-product with acetone could be isolated. In general, carbon tetrachloride has been found to have a greater tendency to form molecular compounds than have ketones or esters. Neither *p*-monobromo-diphenyl-carbinol nor *p,p'*-dichloro-diphenyl-carbinol formed molecular compounds with carbon tetrachloride or acetone at —15°.

Preparation of the Compound $[C_6H_5.C_6H_4.C_6H_5.CHCl]_2.CCl_4$.—When the diphenylmethane derivative was crystallized from carbon tetrachloride at —15° a very unstable addition product was formed. It lost weight rapidly in the air. When kept 20 minutes in an ice-chest the loss on heating was 17.84%. When it was dried rapidly in the air for 2 minutes the loss on heating was 18.66%. The theoretical loss for a compound of the above formula is 21.66%. No molecular compound with acetone could be isolated. Diphenyl-chloromethane gave no compound with carbon tetrachloride.

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