THE RELATIONS BETWEEN STRUCTURE AND SMELL IN ORGANIC COMPOUNDS¹

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The first essential for a smell is, of course, the volatility of a substance. Structural peculiarities and external conditions, which increase the volatility, increase the smell also as a rule. Although the substances with an odor vary very much in their chemical constitution, an examination shows that the large majority of them are unsaturated compounds and that the character of the odor varies with the degree of saturation. Very few substances, containing a triple bond, have a pleasant odor, though propargyl and diacetylene dicarboxylic ester do. In general, substances with a triple bond act so strongly on the nasal passages, and often on the bronchial tubes, that an unpleasantly stifling sensation is caused.

On the other hand, the presence of a double bond is often accompanied by a pleasant odor, as can be seen from the instances² in Table I.

TABLE I

Name	Smell	
Acetacetic ester	Fruity	Liquid
α -Methyl- β -oxyacrylic ester	Pleasant	"
Methyl malonate	Ethereal	"
Ethyl malonate	Aromatic	"
Ethyl oxalate	Spicy	"
Nitric ester	Pleasant	"
Nitroparaffine	"	Solid
Acetonylacetone	"	Liquid
Mesityl oxide	Like peppermint	"
Methyl heptenone	Ethereal	"
Tropylene	Like benzaldehyde	"
Dihydrobenzoic acid	Like cinnamon	Crystals volatile with steam.
Δ_2 -Tetrahydrobenzoic acid	Like valerian	Liquid

¹ Translated from the author's German manuscript by W. D. Bancroft.

² The instances cited throughout this paper are taken from Krafft's "Lehrbuch der organischen Chemie."

TABLE I (Continued)

Name	Smell	
Cantharene	Like terpenes	Liquid
Dihydro- <i>p</i> -xylene	" "	"
<i>l</i> -Limonene	Like lemons	"
Inactive limonene	Pleasant	"
Pinene	Characteristic	"
<i>d</i> + <i>l</i> -Dihydrocarveol	Like terpinol	"
Terpinol	Pleasant	"
Tetrahydrocarvone	Like carvone	"
α -Furfurol	Aromatic	"
Furfuracrylic acid	Spicy	Needles
α -Thiophene aldehyde	Like benzaldehyde	Liquid
Geraniol	Pleasant	"
Linalool	"	"
Citronellal	"	"
Citral	Very pleasant	"
Pseudo-ionone	" "	"

Double bonds are also to be found in ionone, the artificial violet perfume; in irone from the violet roots; and in their derivatives, ionene and irene.

Compounds, containing a benzene ring, show an increase in the smell, especially when the phenyl radical is also connected with a double bond.

TABLE II

Name	Smell	
Phenol	Peculiar	Crystals
Naphthol	Like phenol	Leaflets
<i>o</i> -Chlorphenol	Unpleasant	Liquid
Thymol	Like thyme	Prisms
Creosol	Pleasantly aromatic	Liquid
Mesitylene	Aromatic	"
Cymol	Peculiar aromatic	"
Monochlor-benzene	Aromatic	"
Benzyl chloride	Stifling	"
Diphenyl-methane	Like oranges	Crystals
α -Diphenyl-ethane	Pleasant	Liquids
Tetra-hydronaphthalene	Like naphthalene	"
Nitrobenzene	Like benzaldehyde	"
Benzaldehyde	" "	"

TABLE II (Continued)

Name	Smell	
<i>o</i> -Tolulaldehyde	Like benzaldehyde	Liquids
<i>m</i> - " "	" "	"
<i>p</i> - " "	Peppery	"
Cumene aldehyde	Like cumene	"
Salicylic aldehyde	Peculiar	"
Vanilline	Like vanilla	Needles
Piperonal	Like heliotrope	Leaves
Cinnamic alcohol	Like hyacinth	Needles
α -Chlorstyrol	" "	Liquid
Eugenol	Like pinks, intense	"
Cumarine	Pleasant	Prisms

If the number of double bonds in a compound is increased beyond measure, the effect becomes similar to that of a triple bond. Instead of a plain increase in the intensity of the smell, there is a marked deterioration in the quality, accompanied by unpleasant irritating effects. Instances of this are given in Table III.

TABLE III

Name	Smell	
Acid anhydrides	Stifling	Liquid
Oxymethylene ketone	Penetrating	"
Dihydrobenzaldehyde	Stifling sweetish	"
Quinone	Like ozone	Volatile prisms
Toluquinone	Like quinone	Leaflets
<i>p</i> -Oxyloquinone	" "	Needles
Quinone chlorimide	" "	Volatile crystals
α -Naphthoquinone	" "	Plates

The quinones have four connected pairs of atoms each with a double bond. From the work of Witt, Liebermann, and v. Kostanecki it appears that the color of a substance and the presence of double bonds are connected in such a way that a substance is more intensely colored the more double bonds there are. Now it is remarkable that pairs of atoms with double bonds, 'chromophoric groups', also play an important

part in the case of odoriferous substances and that the increase of chromophoric groups in the molecule, i. e., the presence of 'complex chromophores', causes not only an increase in the color but often an increase in the smell. This surprising relation is especially evident in quinone where the double occurrence in series of the complex chromophore $O:C:C:C$ is the cause of the color and the smell.

The effect of the double bond on the smell is best seen by a comparison of the saturated compounds with the corresponding unsaturated compounds (Table IV).

TABLE IV

C : C	C : C	C : C
Ethane, odorless	Ethylene, faint smell	Acetylene, strong unpleasant smell
Propane, odorless		Allylene, unpleasant smell.
Butane, odorless		Ethyl acetylene, strong smell.
		Dimethyl acetylene, peculiar smell
		Diacetylene, peculiar smell.
		Dipropargyl, strong smell.
Hexane, faint ethereal smell	Diallyl, odor of horse radish	
Propyl alcohol, ethereal smell	Allyl alcohol, pungent smell	
Propyl iodode, pleasant ethereal odor	Allyl iodode, garlic-like odor	
Propyl aldehyde, stifling odor	Acroleine, extremely irritating odor	Propargyl aldehyde worse than acroleine
Isopropyl alcohol, alcoholic smell	Acetone, characteristic smell	
Propionic acid, stifling smell	Acrylic acid, stifling acid smell	
		Propiolic acid, stifling acid smell

TABLE IV (Continued)

C : O	C : O
Butyl alcohol, peculiar smell	Butyl aldehyde, stifling odor
Isobutyl alcohol, peculiar smell	<i>n</i> -Butyric acid, most repulsive smell
Iso-amyl alcohol, peculiar smell	Isobutyric acid, disgusting repulsive smell
Ethyl alcohol, alcoholic odor	Isovalerianic acid, most disgusting smell
Methyl alcohol	Acetic acid, pungent smell
	Acetaldehyde, ethereal but stifling odor
	Formaldehyde, stifling smell
	Formic acid, pungent smell

C : C : C : O

Crotonaldehyde, odor stifling

C : N	C : N
Methylamine, ammoniacal smell	Prussic acid, most stifling odor
Ethylene diamine, ammoniacal smell	Cyanogen, intense odor
Dimethylamine, ammoniacal smell	Methyl carbylamine, frightful and disgusting odor.

From these data it appears that a substance has a more intense smell, the more double or triple bonds it has, or, in other words, the greater the internal tension. Two double bonds on the same carbon atom usually increase the smell of a substance more than a triple and a single bond. This can be seen from a comparison of the isocyanic esters with the normal esters (Table V).

TABLE V

Name	Smell
Normal cyanic esters	Ethereal smelling
Isocyanic esters	Unpleasant smelling, penetrating
Thiocyanic esters	Like garlic
Isothiocyanic esters	Stifling and irritating

If oxygen is replaced by sulphur, the smell becomes more marked and less pleasant (Table VI).

TABLE VI

Name	Smell
Methyl alcohol	Peculiar smell
Methyl mercaptane	Disgusting smell
Ethyl alcohol	Alcoholic smell
Ethyl mercaptane	Most disgusting smell
Phenol	Peculiar smell
Phenyl mercaptane	Intense smell of garlic
Benzyl alcohol	Aromatic smell
Benzyl mercaptane	Garlic-like smell
Acetone	Characteristic smell
Thio-acetone	Unbearable odor
Acetaldehyde	Peculiar ethereal and stifling
Thio-acetaldehyde	Very penetrating odor
Ethyl ether	Ethereal odor
Ethyl sulphide	Disgusting odor
Vinyl ether	Ethereal odor
Vinyl sulphide	Disgusting smell
Phenyl oxide	Odor like geraniums
Phenyl sulphide	Not unpleasant odor
Acetic acid	Pungent odor
Thio-acetic acid	Unpleasant, stifling odor
Carbon dioxide	Odorless
Carbonyl sulphide	Faint smell
Carbon bisulphide	Ethereal smell

Formaldehyde, thioformaldehyde, acetaldehyde and thioacetaldehyde all form odorless polymerization products having three times the molecular weight of the original substance. Since this condensation involves a disappearance of the double bonds, this is an additional proof of the great effect of the double bonds on the smell of a substance. Another instance of this is the polymerization of the volatile and stifling smelling cyanic acid, $O:C:NH$ to the odorless cyanuric acid.

A compound can be unsaturated even when there is no double or triple bond, as for instance when an element does not show its maximum valence. Such compounds have the power of forming addition products just as much as substances containing multiple bonds. As a matter of fact it is hard to

draw a hard and fast line between an unsaturated atom and one that is connected with others by double bonds. It seems to me quite indifferent whether one speaks of a carbon atom with a double or triple bond or whether one says that the carbon atom is trivalent or bivalent. The two are different ways of expressing the same fact, that the substance is unsaturated at ordinary temperatures.¹

Nitrogen is the most important of the elements which may have the same effect on a molecule as the presence of an atomic group with multiple bonds. Thus nitrogen is trivalent in the following compounds, all of which have characteristic smells: ammonia, methylamine, ethylamine, trimethylamine, ethoxyethylamine, *p*-diamidohexamethylene, dimethylene imine, trimethylene imine, pyrrolidine, α,α -dimethylpyrrolidine, piperidine, α -methylpiperidine, α,α -dimethylpiperidine. In a large number of nitrogenous substances we find the occurrence of a multiple bond in addition to trivalent nitrogen. This combination increases the intensity of the smell and often makes its quality worse, just as was the case when many multiple bonds were present in the molecule.

The following instances have already been referred to:

Prussic acid, its normal and iso derivatives.

Cyanic acid, its normal and iso derivatives.

Sulphocyanic acid, its normal and iso derivatives.

Cyanogen, chlorcyanogen, quinone chlorimide.

The following substances in Table VII come under the same head.

¹ If the temperature is raised, unsaturated compounds become saturated, i. e. the power of forming addition compounds decreases. It is a well known fact that acetylene is stable at high temperatures even in an atmosphere of hydrogen, in which it can be formed by the action of the arc. At high temperatures therefore it behaves like a saturated compound which cannot add on any other elements, and there is therefore no sense in writing the formula for ~~acetylene~~ under these conditions with a triple bond, since it has no longer any of the properties which are characteristic of the triple bond.

TABLE VII

Name	Smell
Cyanogen sulphide	Alkyl thionylamines
Acetamide	Diacetone amine
Allyl amine	δ -Propyl- δ -aminovaleraldehyde
Chlor-formamide	Trimethyl isoxazol
Alkyl nitrites	α -Pyrrolidon
α, α' -Methyl pyrrolidon	Pyrrol
Pyrroline	Pyrazol
Methyl glyoxaline	Osotriazol
Triazol	Pyridine
α -Vinyl pyridine	α -Chlorpyridine
β -Ethyl pyridine	α, α -Dimethyl pyridine
β, β -Dimethyl pyridine	Aldehydine
Nitropiperidine	Nicotine
Tropidine	Ketazines
Pyrazine and pyrazine derivatives	Pyrimidine and pyrimidine derivatives
Hydronitric acid	

The combination of unsaturated nitrogen atoms with phenyl or naphthalene radicals causes an increase in the intensity of the smell similar to that caused by the union of atoms with a multiple bond to a phenyl radical. Instances of this are aniline, methylaniline, hydrazobenzene, benzonitrile, diphenylamine, phenylhydrazine, nitrobenzene α -naphthylamine, *ar*-tetrahydro- α -naphthylamine, *ar*-tetrahydro- β -naphthylamine, *ac*-tetrahydro- α -naphthylamine, *ac*-tetrahydro β -naphthylamine.

We may also have the combination of trivalent nitrogen, phenyl radicals, and multiple bonds. It is to be expected that such compounds would have a very intense, usually unpleasant smell. The instances given in Table VIII show that this is true.

The phenyl and carboxyl derivatives of indol are not volatile and are therefore odorless.

What we have shown for nitrogen is probably also true for phosphorus. For the present, however, so few organic phosphorus compounds are available for comparison that we must confine our discussion to the phosphines. The disgust-

TABLE VIII

Name	Smell
Carbanyl	Unbearably stifling
Phenyl mustard oil	Stifling
Anthranil	Penetrating
α -Phenyl triazine	Peculiarly alkaloidal
α -Phenyl isoxazol	" "
Diazobenzene imide	Stupefying ammoniacal
Benzoyl azo-imide	Intense
Benzylidene ethylamine	Stifling
Isoquinoline	Peculiar
Quinoline	"
Methyl quinolines	Penetrating
Acridine	Pervasive
Phenanthridine	Suffocating
Indol	Very unpleasant
Skatole	Faecal-like
Ethylindoxyl	Indol-like
α -Methylindol	" "
α,β -Dimethylindol	" "

ing smell of hydrogen phosphide becomes more penetrating with successive replacements of hydrogen by alkyl, phenyl or toly radicals, and is something fearful in the tertiary phosphines.

This increase in the smell through introduction of methyl groups appears to be a general phenomenon. Not only is the smell of an odoriferous substance increased but substances without smell can be converted in this way into compounds which do smell. Through successive replacements of hydrogen by methyl the smell of ammonia changes into that of pickled herring. Methyl quinone has a more penetrating odor than quinoline; skatole and dimethylindol smell stronger than indol; while the mercaptanes are much more unpleasant than hydrogen sulphide. By substitution we pass from the odorless propane to pentane which has an ethereal odor.

The phenomena with arsenic are similar to those with phosphorus. The most unpleasant smelling compounds are derivatives of trivalent arsenic. Arsenious hydride is more unpleasant than hydrogen phosphide and very much more unpleasant

than ammonia. The arsines are bad-smelling liquids. The cacodyl compounds are very much worse, thus illustrating the effect of the methyl groups. This is the place to refer to the onion-like smell of trimethyl antimonide and to the unpleasant odor of trimethyl bismuthide.

These few phosphorus, arsenic, antimony and bismuth compounds must be considered as unsaturated because the elements appear in their trivalent form. More important, however, than these are the derivatives of bivalent sulphur. A large number of these have already been cited in Table VI. A few more are given in Table IX.

TABLE IX

Name	Smell
Thiophene	Characteristic
Thienyl sulph-hydrate	Most unpleasant
Thiophene alcohol	Faintly aromatic
Thiophene aldehyde	Like benzaldehyde
Thiophthene	Tarry
Oxythionaphthene	Like phenol

It is to be noted that the invariable impurity of benzene, thiophene, is changed by the addition of an aldehyde group, just as benzene is, into a substance which smells like the oil of bitter almonds. This might be looked upon as a mere accidental coincidence were it not for the fact that the other derivatives of thiophene smell very like the corresponding benzene and naphthalene derivatives, as may be seen from Table X.

TABLE X

Name	Smell
Naphthalene	Peculiarly tarry
Thiophthene	Tarry
α -Naphthol	Like phenol
Oxythionaphthene	" "
Benzyl alcohol	Aromatic
α -Thiophene alcohol	Faintly aromatic
Phenyl mercaptane	Most unpleasant
Thienyl sulph-hydrate	" "

It appears almost as though the sulphur atom were capable of replacing two CH groups without causing any essential change in the smell or other properties of a compound. This similarity of properties would be of course the reason for the difficulty in separating benzene from thiophene, and toluene from methyl thiophene. All the compounds in which sulphur has its lowest valency are characterized by a more or less intense and unpleasant smell. If one compares with these the compounds in which sulphur is either quadrivalent or hexavalent, it appears that these latter are either odorless or have a relatively pleasant smell as in the case of the alkyl esters of sulphurous and sulphuric acids. In the esters of sulphurous acid there is one double bond while there are two in the esters of sulphuric acid. A natural consequence of this is that the smell is more intense in the odoriferous derivatives of sulphuric acid than in the corresponding derivatives of sulphurous acid. Sulphur dioxide, however, has a very irritating effect; but it has two double bonds.

It has already been pointed out in this paper that the sulphur compounds usually have more of a smell and a worse smell than the corresponding oxygen compounds. This may be explained on the basis that substances with bivalent sulphur are unsaturated even when there are no double bonds and that the bivalent sulphur increases the effect of double bonds, when present, just as trivalent nitrogen increases the effect of multiple bonds.

Lately, the view has been gaining ground that oxygen is quadrivalent in some compounds. In that case one could ascribe the odor of alcohols and ethers to the presence of an unsaturated oxygen atom. That substances containing oxygen have a less marked smell than those containing sulphur would then be explained on the ground that bivalent sulphur is much more unsaturated than bivalent oxygen, as shown by the lesser readiness of the latter to assume and hold a higher valence.

Even if one were satisfied with this explanation for the odor of alcohols and ethers there still remain many substances

which are undoubtedly saturated and which yet smell. A striking case of this is hexachlorethane which smells like camphor and which crystallizes in plates that are volatile in the air. The following substances also have a camphor smell: camphor, trimethyl carbinol, acetone chloroform, dimethylallyl carbinol and higher alcohols of this series, durol, borneol, methyl tertiary butyl carbinol, ethylidene malonic acid, silicon tetra-ethyl, and silico-heptyl alcohol. While these substances, which smell like camphor, belong to all sorts of different classes, they all have one peculiarity in common, at least one carbon atom in which the hydrogen has been completely replaced by other groups. In every case at least two and usually three of the substituting groups are identical. The methyl group appears most often as a substituting group and chlorine is fairly well represented, while in one case there are two carboxyl groups and a double bond.

The presence of the double bond appears to be unimportant. The character of the fourth substituting group is of little importance except when it acts strongly against the other three. The effect of a negative carboxyl group, for instance, weakens the effect of three positive methyl groups.

Essential for the existence of a smell like camphor is the complete substitution of all the hydrogen attached to a carbon atom and the substituting groups should be as much alike as possible. In this way the intramolecular repelling forces become especially great and the increase of the internal pressure causes a maximum volatility.

A strong smell is characteristic of all substances in which a carbon atom is overloaded with identical groups, either positive or negative. This is brought out in Table XI.

TABLE XI

Name	Smell
Chloroform	Strongly ethereal
Bromoform	" "
Iodoform	Characteristic
Trichloronitromethane	Stifling
Chloral	Pervasive
Chloral hydrate	Peculiar
Dichlor-acetone	Pungent
Thiocarbonyl chloride	Suffocating
Perchlor methyl mercaptane	Unpleasant
Ethylidene chloride	Ethereal

In harmony with this is the fact that normal alkyl derivatives of a substance almost always have a fainter odor than the iso derivatives while these have a fainter odor than the corresponding tertiary compounds (Table XII).

TABLE XII

Name	Smell
<i>n</i> -Valerianic acid	Repulsive
Isovalerianic acid	More repulsive
Trimethyl acetic acid	Stifling acid
<i>n</i> -Butyl alcohol	Peculiar
Secondary butyl alcohol	Intense
Isobutyl alcohol	Unpleasant
Tertiary butyl alcohol	Like camphor

Artificial musk, one of the most strong smelling substances, has a carbon atom united to three methyl groups. A carbon atom overloaded with methyl groups is to be found in the hydrocyclic compounds (Table I); in the most closely related aromatic substances (Table II) such as cymol, thymol, carvacrol and others; and in the related substances with open rings such as citral, etc. Most of the perfumes come under the mentioned heading of substances which combine great volatility with the property of affecting the nasal passages pleasantly. The volatility is brought about by the overloading of the carbon atom with methyl groups while the scent is due to the presence of double bonds.

The closing of the ring is only of minor importance both in regard to smell and to other properties. The pleasant odor of the terpenes and their oxygen derivatives remains after the ring is broken. As an instance we may take the often-cited citral and compare it with pulegone. In other types the slight effect of closing the ring can be shown (Table XIII).

TABLE XIII

Name	Smell
Tetra methyl carboxylic acid	Like fatty acids
<i>n</i> -Valerianic acid	Repulsive, sour
Pentamethylene carboxylic acid	Sour
<i>n</i> -Caproic acid	"
Hexahydrophenol	Like fusel oil
<i>n</i> -Amyl or capryl alcohol	" " "
Diethylamine	Ammoniacal
Pyrrolidine	"
Ethyl acetamide	Like acetamide
α -Pyrrolidon	" "

Cases may, however, arise in which the closing of the ring has an effect. This will happen when the closing of the ring is accompanied by a marked increase in the internal tension. Thus trimethylene has a faint smell while propane is odorless. Erythrit ether has a pleasant odor while erythrit has practically no smell. Glycidic acid has an irritating smell which does not occur in glyceric acid. The same contrast is to be found between the sharp smelling propylene oxide and propylene glycol. In di- and tri-methylene imines an accentuation of the ammoniacal smell can be noticed, as compared with dimethyl- and methyl-ethylamine. Dimethyl ketone and its lower homologues have an aromatic smell which changes to a strong odor of peppermint in di-tetra methylene ketone.

According to Baeyer's tension theory it is to be expected that the closing of the saturated five-membered ring would have the least effect on the properties and especially on the smell because the system closes without perceptible change in tension. So far as is known, the facts are in accord with this view.

The closing of the six-membered ring and still more of the seven-membered ring causes, however, an increase in tension which shows itself in an increase in the odor. Ethyl propyl ketone and dipropyl ketone smell like acetone. On changing into keto-hexamethylene and suberone respectively, a strong smell like peppermint is developed precisely analogous to what can be observed in the closing of the ring with ditetramethylene ketone. The sign of the tension change in ditetramethylene ketone is, however, the opposite of that for keto-hexamethylene and suberone. In addition, it is to be noted that the closing of the ring always has an immense effect upon the odor if the multiple bonds of a system are affected thereby, as in the case of paraldehyde or cyanuric acid.

A few anomalous cases must now be discussed. It has been shown that multiple bonds usually cause the smell and that the intensity of the smell increases with increasing accumulation of multiple bonds. Quite apart from unsaturated side chains, benzene derivatives possess three double bonds while the di- and tetra-hydro addition products have two and one respectively. We should therefore expect the genuine benzene derivatives to have a more noticeable odor than the hydrogen addition products. This is by no means the case, as may be seen from Table XIV.

TABLE XIV

Name	Smell
Benzene	Peculiar
Dihydrobenzene	Garlic-like
Tetrahydrobenzene	" "
Benzoic acid	Peculiar
Dihydrobenzoic acid	Like cinnamon
Δ_2 -Tetrahydrobenzoic acid	Like valerian

Also carvomenthol, with its odor of orange blossoms, and other hydrocyclic compounds have a stronger smell than the corresponding aromatic compounds, such as carvacrol for instance.

This peculiar behavior agrees also with other observations wherein benzene behaves in many respects as though it were more saturated than the really unsaturated di- and tetra-addition products (Thiele).

As a matter of fact these and other observations have caused some people to draw the conclusion that there are no double bonds in benzene. This conclusion is unquestionably right if one looks upon a 'double bond' as something unchangeable. There are, however, no conclusive reasons for assuming the unchangeability of the state which one calls the double or the triple bond. The facts favor the opposite view that we have to deal with something changeable, which depends on temperature, pressure and the nature of the substituting groups. The degree of saturation and consequently the number of 'bonds' varies with the conditions. There are cases known in which the constitution of the substances shows that they unquestionably contain double bonds and yet a suitable substitution will cause these substances to lose their power of adding on substances. This power to form addition products can also disappear with rising temperature, as has already been pointed out. Such substances behave exactly as though they were saturated compounds and that is probably what they are.

Something similar is obviously true for benzene, whose three double bonds are modified by cross connections and so bring about a very peculiar state which is half way between that of a saturated and an unsaturated compound.

Another anomaly is to be found in compounds of the uric acid group. The molecule of uric acid is composed entirely of groups which increase the odor; namely, three carbonyl groups, one ethylene group, and four unsaturated or trivalent nitrogen atoms. In spite of this, uric acid is entirely odorless and, in spite of four chromophoric groups, it has no color. It is quite possible that these remarkable phenomena are connected with the fact that a decrease in the refraction and dispersion takes place when the carbonyl group is united directly

to the amino group (*Zeitschrift für physikalische Chemie*). The decrease in the refraction and the dispersion constants would be significant of an approach to a saturated state. The cause of the decrease in the constants and especially of the absence of smell is perhaps to be found in the fact that the carbonyl group has a markedly negative character while the amino or imino group is strongly positive. The attraction between these two opposing complexes may decrease the volatility for this is on the other hand increased by the presence of two like, and therefore mutually repelling, groups. This molecular attraction between positive and negative parts of a molecule is possibly also the reason why metallic salts of volatile acids are not volatile and are therefore odorless.

Mention must also be made of the odoriferous saturated compounds which show a normal structure and apparently no overloading of a carbon atom with identical groups. Among such substances are pentane, hexane and heptane which are all very volatile and which all have a noticeable ethereal odor. Other instances are the methyl halogen compounds, CH_3Cl , etc. If one writes the formulas for these compounds a little differently, pentane becomes a diethyl methane, hexane an ethyl propyl methane, and heptane a dipropyl methane. The odor of pentane and heptane would be explicable on the basis of two identical groups attached to the same carbon atom. The odor of hexane is much fainter, as was to be expected from the substituting groups being similar but not identical.

The smell of the saturated secondary alcohols and ethers can be explained in the same way if one does not care to fall back on the unsaturated oxygen atom.

The volatile monohalogen derivatives of the saturated hydrocarbons, methyl fluoride, methyl chloride, methyl iodide, and also the primary alcohols are characterized by the fact that the hydrogen combined with the halogen in the halide acid or with the hydroxyl in water has been completely replaced by a methyl or a homologous alkyl group. These compounds are therefore to be classed with those in which a

complete substitution of hydrogen by alkyl groups has occurred. The only difference is that there is only one replaceable hydrogen atom in a halide acid. The behavior of these halogen compounds could also be explained as due to an unsaturated halogen, since the halogen may have a valence of seven.

The most important results of this paper may be summed up as follows:

1. An odoriferous substance must be volatile.
2. An odoriferous substance may be a saturated or an unsaturated compound. The first case is rare and the smell is then perceptible only when the substance is extremely volatile.
3. The volatility is increased especially by overloading a carbon atom with identical groups. Substances, in which all the hydrogen of at least one carbon atom has been replaced, often have an odor like camphor when at least two of the substituting groups are identical. Such a system has the maximum volatility. Under these circumstances it is indifferent whether the compound is saturated or unsaturated, though three of the substituting groups must be the same if the compound is saturated. The nature of the fourth is important only when it works against the other three.
4. The combinations of groups which increase the volatility and smell of saturated compounds act similarly in the case of unsaturated compounds.
5. Everything else being the same, the odor of a compound increases in intensity as the degree of saturation decreases.
 - 5a. Substances with a triple bond usually have a more marked odor than substances with a double bond.
 - 5b. The presence of several double or triple bonds increases the smell.
 - 5c. Presence of an unsaturated atom may also be the cause of a substance having a smell.
 - 5d. The combination of unsaturated atoms and of mul-

tiple bonds increases the smell just as does the presence of several multiple bonds.

5e. The greatest increase in odor is obtained when the same substance has multiple bonds, unsaturated atoms, plain or hydrogenized phenyl or naphthalene radicals, and carbon atoms all of whose hydrogens have been replaced.

6. It may happen that a combination of groups may nullify the smell even when each group by itself would increase it. This occurs with the uric acid compounds where electropositive imido groups are attached to electronegative carbonyl groups. The mutual attraction of these complexes causes a pressure exerted inwards while a pressure exerted outwards is essential to volatility. This latter tension can obviously be obtained through the repelling action of similar groups.

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