# A STUDY OF MERCAPTAN CHEMISTRY

WILLIAM MARIAS MALISOFF, ERNEST M. MARKS, AND FRED G. HESS

*The Atlantic Refining Company, Philadelphia, Pennsylvania*

*Received August 28, 1930*

The study of sulfur compounds represents a relatively neglected page of organic chemistry. In at least two directions its importance is becoming felt more and more strongly,—the field of industry and the field of biochemical research. The recognition is rife that many raw products, such as petroleum, shale oil, tars, etc., contain a wide variety of sulfur compounds which imperatively demand removal and utilization. Equally pressing is the discovery that sulfur compounds play a prominent part in organic metabolism, where the —SH group achieves a fundamental rôle hitherto not fully realized.

We have chosen for discussion the more restricted field of mercaptan chemistry, using the old term "mercaptan" in the wider sense of any compound containing one or more —SH groups. Our objectives in this paper are: (1) a critical presentation of the accumulated data in this field, (2) a discussion of the results of such a presentation, and (3) the outlining of outstanding research problems that suggest themselves to active workers in this field.

We propose to treat the subject of mercaptan chemistry under the arbitrary but systematic headings of the following outline:

I. Physical Characteristics
II. Chemical Characteristics
III. Method of Preparation and Purification
IV. Detection and Determination
V. Special Interest Attaching to the Substances
VI. Research Problems

The subheadings will become apparent in the discussion. Our chief objective is to point out the essential facts and to indicate

their continuity with the corresponding facts of better known analogous compounds, such as the alcohols, phenols, etc. At the same time novel features and unsolved problems are bound to come to light. An effort, therefore, will be made to present speculative discussion right on the heels of the facts, with the hope of at least raising questions even if no final answer can be given.

## I. PHYSICAL CHARACTERISTICS

### *1. General appearance*

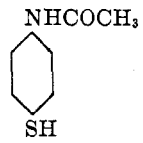
*Physical state.* Methyl mercaptan (1) appears to be the only normally gaseous member of the type RSH, where R is substantially any type of radical. Hydroxymethyl mercaptan (2), however, is a solid. The aliphatic mercaptans, in so far as they have been prepared, are liquids. Yet, $\beta$-aminoethyl mercaptan (3) is a solid. It may be surmised that substitution of groups in the molecule has quite a marked effect on the physical state.

Comparing mercaptans with corresponding oxygen compounds in regard to physical state reveals some differences. There are no gaseous members in the oxygen series. In the sulfur series thiophenol, *o*-thiocresol and $\alpha$-naphthyl mercaptan are liquid (4); in the oxygen series the corresponding compounds are solid. *p*-Thiocresol and *p*-cresol, however, are both solids (5). The trend, of course, is more distinctly brought out in the data on melting points and boiling points.

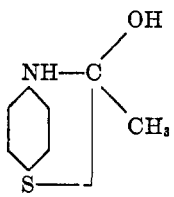
*Crystal structure.* There is a general dearth of data in this field, though vague descriptions abound in which reference is made to "needles," "leaflets" or "platelets." Where a series of compounds has been observed, e.g. the thiosulfocarbamates, NH =C(SH)SR (6), there is no consistency or continuity in crystal structure among homologues. Studies of the simpler members of the aliphatic series should be of interest, but are still unavailable.

*Color.* Aliphatic mercaptans are almost exclusively colorless. This is so consistently true that any description of a preparation as "yellowish" would throw doubt on its purity. Thiophenol, the thiocresols and the naphthyl mercaptans (4, 7) are colorless,

and it is possible that other members of the aromatic group are not as yellow as they have been reported to be. On the other hand, it is quite evident that in a case like that of *p*-acetaminothiophenol, two varieties may exist, one colorless and the other yellow (8). The colorless variety would be



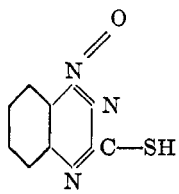

and the yellow,




Phenyl $\beta$, $\beta'$-dimercaptovinyl ketone,

$$C_6H_5COCH : C(SH)_2,$$

gold yellow platelets, may also be a case similar to that of *p*-acetaminothiophenol, although the existence of two forms has not been noted (9). Heterocyclic types furnish us with cases where a decided color may be expected. Thus, phentriazoxine mercaptan

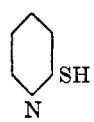



forms red needles (10). *o*-Quinolyl mercaptan (11) is also red.

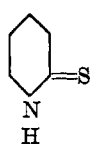
More complex forms, as $\alpha$-mercapto-$\beta$-carbethoxythio-$\gamma$-pyrone-$\beta_1$- hydroxythiophene, show different crystal forms of different color, as orange-red prisms and yellow needles, depending on

possible internal rearrangements (12). In any case the rôle of an —SH group in conferring color properties is apparently very similar to that of an —OH group (13). We should like to suggest that a close examination of the question would reveal that contamination with disulfides may have led to erroneous observations on color in quite a few cases, and that more analogies with hydroxy compounds will be borne out as undue complicating factors of complexities of structure are ruled out.

*Odor.* The unpleasantness of the odor of the mercaptans is proverbial. The odors have been referred to as "evil," "provoking," "unbearable," "furchtbar," and the like. It is hard to see how one observer specifies thiophenol as having a garlicky, but "not unpleasant" odor (7a); but *de gustibus non est disputandum.* Nonyl and decyl mercaptans rise almost to the status of perfumes. Decamethylene thioglycol has been approved (14). *p*-Phenylene dimercaptan has a "peculiar odor" (15), while β-thioanthrol, myricyl mercaptan, *o*-quinolyl mercaptan and *o*-xylylene dimercaptan are completely odorless (16, 16a, 16b, 16c). The parallelism with hydroxy compounds is evident in spite of prejudice. It is possible, we have noted, to detect the choking effect of the butyl and amyl alcohols in the corresponding mercaptans. In some cases curious cancellations occur, as in pyridine mercaptan, which is almost odorless (17). There is some evidence that marked odor changes may be due to tautomerism. We may expect an equilibrium between



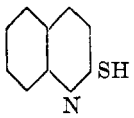

and



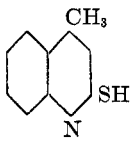

the latter yielding derivatives of ferocious odor. Should some such considerations rule this field there may be in it a rich har-

vest for the "Riechstoff" chemist, and, perhaps, the psychologist as well.

*Taste.* Either unusual courage or accident has produced the observations that *o*-quinolyl mercaptan,




is tasteless and




is bitter (16b). Myricyl mercaptan is also tasteless (16a). Thioglucose has a sweet but unpleasant taste (18). Since these compounds have no characteristic odor, they may perhaps find some use for abnormally jaded appetites.

*Miscellaneous.* A direct, fast, orange dye is available in *o*-quinolyl mercaptan (16b).

### *2. Identifying constants*

*Density.* The density data reported are of no high order of reliability. For aliphatic mercaptans they merely indicate a range of 0.833–0.894 without any consistent regularity, probably due to experimental error. The aromatic mercaptans are in general heavier than water. The thioglycols are also heavier (19). This is in general agreement with hydroxy compounds.

*Thermal constants.* (*a*) *Boiling points and melting points.* The usual chaos of data exists with regard to melting and boiling points. Thus, ethyl mercaptan is reported to melt at −121°C. as well as at −144° (20). It may be suggested that hydrate formation is probably a factor in some cases. An interesting instance is that of *o*-quinolyl mercaptan with two molecules of water of crystallization. It melts at 58–9°, and in a desiccator gradually changes to a violet liquid (11). The hydrate is solid, the anhydrous compound is liquid.

The boiling points of mercaptans are generally consistently lower than those of the corresponding alcohols or phenols or glycols. A convergence becomes apparent for higher homologues

TABLE 1

*Comparison of the boiling points of some mercaptans with those of the corresponding hydroxy compounds*

| RADICAL ATTACHED TO THE -SH OR -OH GROUPS | MERCAPTAN | HYDROXY COMPOUND |
|---|---|---|
| | *Boiling point in °C.* | *Boiling point in °C.* |
| Methyl (21) | 5.8–7.6 | 66 |
| Ethyl (22) | 34.7–37 | 78.4 |
| *n*-Propyl (23, 22a) | 65 –68 | 97.4 |
| Isopropyl (22a) | 53 –59 | 82.8 |
| *n*-Butyl (24, 23, 22a, 21) | 96 –98 | 117 |
| Isobutyl (22, 22a) | 86.6–88 | 106.5 |
| Isoamyl (25, 22) | 116.6–122 | 130 |
| *n*-Hexyl (26, 22a, 21) | 145 –8 | 157 |
| *n*-Heptyl (22a, 21) | 174 –5 | 175.8 |
| Ethylene (27) | 146 | 197–197.5 |
| β-Phenylethyl (28) | 105 at 23 mm. | 212 |
| γ-Phenylpropyl (28) | 109 at 10 mm. | 235 or 119 at 12 mm. |
| Propylene (19) | 152 | 188 |
| Trimethylene (19) | 169 | 214, 227 |
| Allyl (29) | 90 | 96.6 |
| Phenyl (30, 5) | 166 –170 | 182.6 |
| Tolyl (in *o* position) (5) | 194 –195 | 190.8 |
| Tolyl (in *p* position) (31) | 190.2–191.7 | 201.8 |
| Benzyl (32) | 165, 194–5 | 204.7 |
| *m*-Xylylene (33) | 157–8 at 15 mm. | 1, 3, 2.....211.2<br>1, 3, 4.....211.5<br>1, 3, 5.....219.5 |
| Naphthyl (-SH or -OH in position 1) (5) | 285 | 278–80 |
| Naphthyl (-SH or -OH in position 2) (34, 7) | 153–4 at 15 mm.<br>286 at 760 mm. | 285–6 |
| Furfuryl (-SH or -OH in position 2) (35) | 155 | 168–70 |

where the effects of other groups predominate. The few instances given in table 1 will suffice to show this. The curves in figure 1 give a comparison of the boiling points of some mercaptans with those of the corresponding hydroxy compounds.

It is our opinion that the differences are not to be explained merely on the basis of different degrees of association, since in some cases the values of the two series are too close and in a few instances the relations are actually reversed.

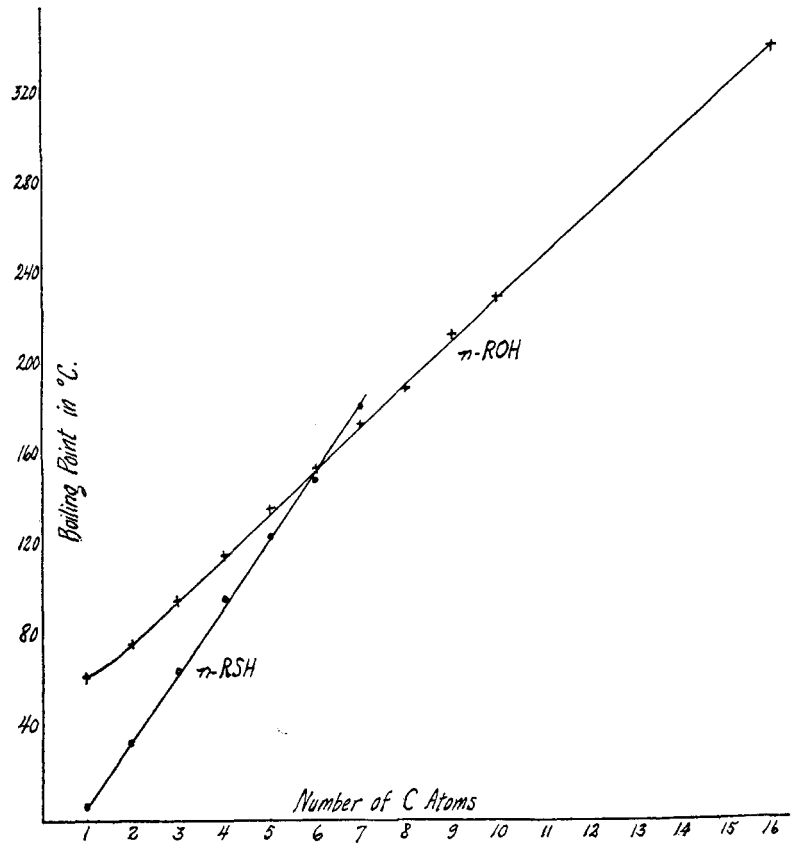


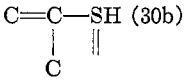

FIG. 1. BOILING POINTS OF SOME MERCAPTANS AND OF THE CORRESPONDING HYDROXY COMPOUNDS

(*b*) *Heats of combustion and of formation.* This is a promising but much neglected field. Several measurements have been made. Reference can be made (36) particularly to some experiments and calculations tending to show that the secondary val-

ences of sulfur in RSH are much less than those of oxygen in ROH (alcohols). The procedure involved the measurement of the heats of formation of the addition compounds formed by the given compound and the Grignard reagent, ROMgI. These results were checked by displacement of the sulfur compounds by the corresponding oxygen compounds. The heat of formation of the sulfur compounds and the heat of displacement by the oxygen compounds together equal the heat of formation of the oxygen addition compounds. In this way, the secondary valences of sulphur and oxygen are compared. The explanation is probably connected with the gradual increase in basicity as we go through the series sulfur, oxygen and nitrogen.

(*c*) *Other thermal data.* Other thermal data, as specific heats, latent heats and the like, seem to be entirely lacking. There are a few isolated measurements on the variation of vapor tension with temperature (37) and a few determinations of critical temperatures (38, 22c, 22d), the latter being somewhat lower than for oxygen compounds. Ethyl mercaptan has been reported as forming mixtures of minimum boiling point with *n*-pentane and trimethylethylene (39). A harvest of analogies, involving matters coming in contact with theoretical issues, is quite certain to be discovered in this field.

*Optical constants.* Refractive indices have been obtained for only a few mercaptans (40, 22, 19a, 5). These yield a value of 7.76 for the atomic refraction of sulfur (21), thus checking results on other sulfur compounds. Estimates have been made on very limited data of the optical exaltation of the grouping




Optically active amyl mercaptan has been studied slightly (41), and mutarotation has been observed for glucothiose (42). Absorption spectra of phenol and thiophenol have been compared (43). In spectra of the vapor the chief contrast is a shift from some 70 bands for phenol to 2 weak bands for thiophenol at 2870 and 2798. On the basis of such facts it would be difficult to

develop any method of detection of thiophenol in phenol, but probably phenol in thiophenol would be easily noted. Many interesting possibilities come to mind which would have theoretical as well as practical utility, but there is still very little to be gathered from the scanty observations except that both positive and negative analogies must be plentiful.

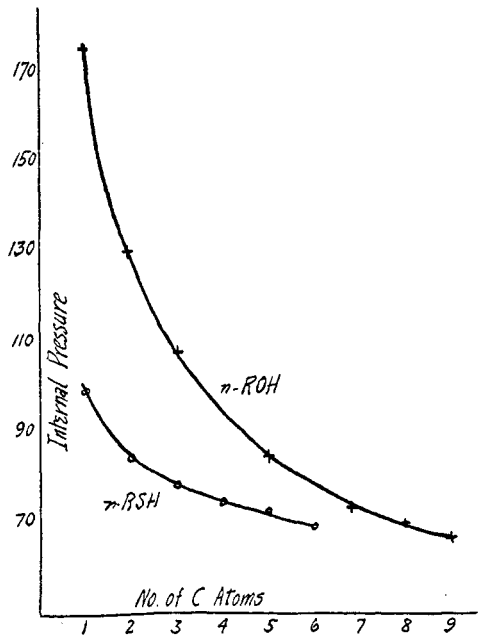



FIG. 2. INTERNAL PRESSURE OF SOME MERCAPTANS AND OF THE CORRESPONDING HYDROXY COMPOUNDS

*Electrical constants.* Measurements of conductivity are available in some cases for thio acids, showing an increasing acidity on the replacement of sulfur for oxygen (44). It is taken for granted that mercaptans are more acidic than alcohols and phenols, but it is not known how much more acidic they are on the basis of conductivity or just where they stand in mutual relation. Furthermore, the effect of substituting groups may be quite different in the sulfur series as compared with the oxygen series. There is no *a priori* reason for assuming additivity effects.

*Miscellaneous constants.* We have charted a series of values for the internal pressure of mercaptans (see figure 2) comparing them with the alcohols, according to the empirical formula:

$$\text{Internal Pressure} = \frac{5200 + 30\ T}{\text{Molecular Weight}} \times \text{Density at } 20°\text{C.},$$

where T is the boiling point in °C. (45).

To complete our list we will mention some isolated viscosity measurements (46, 19a). Ethyl mercaptan shows higher values than ethyl alcohol, but mixtures of the two give still higher values. The "adhesional work" between ethyl mercaptan and water has been measured (47). It is less than that for ethyl alcohol. An internal pressure of 1490 atmospheres is reported, and $\gamma_\sigma$ in the Ramsay-Shields formula is 18.95 (48). These results may be of some value in the study of solubility. Fragmentary data on cryoscopic behavior of phenyl mercaptan in phenol are also reported (49).

### *3. Distribution data*

*Solubility in various solvents.* In the matter of solubility considerable contrasts are to be found between mercaptans and alcohols and phenols. The aliphatic mercaptans are insoluble in water except for such compounds as hydroxymethyl mercaptan (2) and β-aminoethyl mercaptan (3) which have solubilizing groups. Ethyl mercaptan at the same time forms a crystalline hydrate below 8° (50). The matter, however, is complicated by contradictions among observers. Thus, monothioethylene glycol is reported as slightly soluble (51), and also as completely miscible (51a, 19a). The contrasts between sulfur and oxygen types, however, are more likely. Compare for instance, the fact that *p*-nitrothiophenol is easily soluble in water (52), with the fact that *p*-nitrophenol is soluble only with difficulty.

In alcohol the solubilities of most simple mercaptans are consistently high. Moderate solubility is shown by triphenylmethyl mercaptan (53). More complex types, such as phentriazoxine mercaptan (10) and β-thioanthrol (16), are difficultly soluble. This contrasts again with the very high solubility of triphenylcarbinol and of β-anthrol in alcohol.

A further contrast in solubility is found in the fact that β-thioanthrol is not very soluble in ether, whereas β-anthrol is. Triphenylmethyl mercaptan (53) is only moderately soluble in ether, the corresponding carbinol being very soluble. Otherwise ether is an excellent solvent for mercaptans as well as for alcohols and phenols. The same apparently applies to benzene, and probably, to judge from scanty data, to carbon disulfide and chlorinated solvents.

A phenomenon of color change on solution is to be found in the case of ana-bromo-*o*-quinolyl mercaptan (11), yellow in the solid state and reddish in acetone. This resembles the color change often noted in the case of disulfides. This factor is here eliminated because the disulfide is white. It is probable that more such cases will be discovered and that their explanation would point to some form of association with the solvent.

*Adsorption, diffusion, partition, etc.* No quantitative data have been published in the literature, though patents abound on the adsorption of mercaptans by metallic sulfides (54). In particular the activity of cupric sulfide is receiving some attention at present.

Partition studies are scarce. The distribution between hydrocarbon solvents and various strengths of caustic soda, at least for the aliphatic series (55), has been taken up on account of the commercial urgency of the issue. The mercaptans are very weak acids indeed, and are largely inextractable and become totally inextractable as the molecular weight increases. A curious datum is the reported solubility of *secondary* hexyl mercaptan in potassium hydroxide of specific gravity 1.22 and its separation into two layers at higher temperatures (56). This may be due, however, to increased hydrolysis of the potassium mercaptide formed, and not to any pure distribution phenomenon.

To summarize the state of our knowledge as to the physical characteristics of mercaptans, we should like to point out that the field is a fertile one for further study. There is a total, or almost total, lack of data on dielectric constants, conductivity, internal pressure, vapor tension, thermal constants necessary for thermodynamic calculation, and optical measurements. Many cor-

rections of the available data are needed. Distribution data in particular require re-working on a quantitative basis.

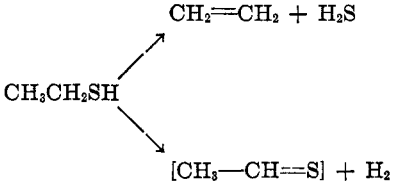
## II. CHEMICAL CHARACTERISTICS

### *1. Stability and decomposition*

*Thermal.* Little has been done along the lines of a detailed systematic study of the thermal stability of mercaptans. The evolution of hydrogen sulfide has been noted, and the formation of other products more or less guessed at (57, 51, 16). Therefore, we find both sulfides and disulfides and even elementary sulfur referred to. Then again catalysts seem to affect the reaction markedly (58). As to the decomposition of metal derivatives of mercaptans there is also disagreement. In the case of lead and similar mercaptides some authors write reactions showing only sulfide formation; others include the formation of some free mercaptan (59, 23, 7). There is also no doubt that mild decomposition sets in even under conditions of steam distillation in many cases, especially with the higher aliphatic members (60, 22a).

More should be done to segregate stable types from unstable ones. Thus thio acids, carbithionic acids (57l) and complex mercaptans belong to the latter group. Particularly unstable are the mono-, di- and tri-thioglycerols, hydrogen sulfide being given off even below 100°. Triphenylmethyl mercaptan also shows ready decomposition. Occasionally a very special case turns up, such as that of 2,4,6,-trinitrothiophenol which explodes similarly to picric acid (57d).

As a matter of fact—and our own unpublished work supports it strongly—by analogy with the alcohols one should expect olefin formation along with hydrogen sulfide, and, in the presence of some specific catalysts, hydrogen formation along with thio aldehydes. This has been surmised also by Hurd (61) who formulates the possible reactions:



The thioacetaldehyde, he speculates, may form tetraphenylthiophene. We have not found this latter speculation to be true. In general, olefin formation for the aliphatic types is predominant, and stability decreases with increasing molecular weight. The aromatic types are less stable than the aliphatic and probably follow a different course of reaction.

*Electrical decomposition and dissociation.* No direct data are available. A few electrolytic oxidations, limited to thiourea types in which disulfides are formed, would indicate the existence of an anion due to slight dissociation as acids (62).

*Photochemical decompositions.* No data were found concerning photochemical decompositions.

*Miscellaneous:—tautomerism, rearrangements.* In the study of the stability of compounds containing the —SH group one must keep in mind the possibilities of tautomerism and rearrangement. We may cite the case of thiocarbanilide (63), the ordinary formula of which is

$$S{=}C(NHC_6H_5)_2,$$

but which behaves with halogen alkyls as if it were

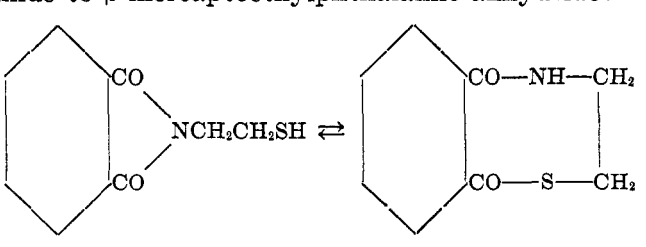
$$C(=NC_6H_5)(SH)(NHC_6H_5).$$

This is general for the group

$$\begin{array}{l} S \\ \| \\ -C-NH \end{array}$$

as in thiourethans, thiosemicarbazide, etc. (64).

Very similar is the reported tautomerism of thioacetamide caused by iodine (65). Cases more removed from these types are illustrated by the rearrangement (3) of $\beta$-mercaptoethylphthalimide to $\beta$-mercaptoethylphthalamic anhydride:



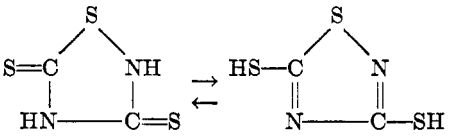
*p*-Acetaminothiophenol also shows two forms, one yellow and stable, the other colorless and labile (8).

A type of change recently discussed is the equilibrium between esters of dithiocarboxylic acids and pseudo acids (44):

$$RC(:S)S \cdot C_nH_{2n+1} \rightleftarrows RC(:S)SH$$

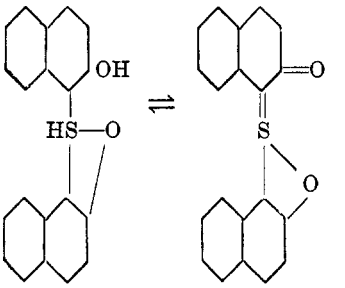
These pseudo acids form pseudo salts.

Similar considerations apply to perthiocyanic acid which may be pictured in two forms (66):



Pseudo form Labile form

The —SH group also gives rise on occasion to the so-called "thionylium ring" (67), as illustrated by aromatic *o*-hydroxysulfides:



Isosulfide Dehydrosulfide

In this connection we should like to point out that such studies are very likely to assume an important rôle in the investigation of the biological equilibrium of complex organic compounds containing an —SH group. Dextro and levo isomers of mercaptans and their Walden inversion are already attracting some attention (68).

*2. Formation of addition compounds*

A crystalline hydrate of ethyl mercaptan has been reported (50). There seems to be no reason why other mercaptans should not form hydrates also. Some parallelism, too, may be found in the consideration that mercaptides often form hydrates (69). Nevertheless, the possibility, suggested by analogy, of the addition of hydrogen sulfide instead of water has apparently not been tested.

Unsaturated hydrocarbons form addition products. Phenyl and benzyl mercaptans add to styrene, 1,1-phenylmethylethylene, trimethylethylene and some terpenes (70). When compounds like benzylidene benzoyl acetone or cinnamylidene acetophenone, representing a very large variety of unsaturated ketones and diketones, are found to add mercaptans it is due, no doubt, to their functioning as unsaturated hydrocarbons (71). In conformity with expectation in such cases the mercaptan residue adds to the most hydrogenated carbon atom.

Addition reactions have been reported for halogenated hydrocarbons with mercaptans of the type of *o*-quinolyl mercaptan and the so-called thio amides (72). It is interesting to note that the same types form double salts with mercury, platinum, zinc and lead halides (73, 16b). This suggests a probability that similar cases would be forthcoming amongst mercaptans containing heterocyclic rings, e.g. imidazole mercaptan and its derivatives. Perhaps we may include in this set "chloral phenyl mercaptan," which is a definite individual, and a series of addition compounds formed preliminary to condensation between chloral and monothioethylene glycol or halogenated aromatic mercaptans (74).

A reaction quite analogous to the addition of aldime (HCl·HCN) to phenols and phenol ethers is brought out in the case of all mercaptans, including the aliphatic types (75). Iminothioether hydrochlorides are formed. The addition is of even wider significance, since in the presence of hydrogen chloride the place of hydrogen cyanide can be taken by acetonitrile, phenyl nitrile, benzyl nitrile, trichloroacetonitrile, and phenylene dinitrile (76).

Additions with various quinones, phenanthraquinone and chrysoquinone have been found, in particular for *n*-butyl, amyl, benzyl and phenyl mercaptans (77). This is analogous to the addition of phenols to quinone. We should also expect, therefore, similar reactions for polymercaptans, since the reaction occurs for polyphenols.

Observations have also been made on the addition of unsaturated acids, such as acrylic and cinnamic acids, and ketonic acids, such as pyroracemic acid, to aromatic mercaptans (74a). There are, however, quite a few irregularities and exceptions which in themselves should prove interesting. Both aromatic and aliphatic mercaptans seem to add to isatin and its derivatives. Compounds with ethylene oxide have been found (79). A group of mercaptans of the type of β-aminoethyl and β-methylaminoethyl mercaptans, are characterized by picrate formation (3). An odd case is the formation of an addition compound of ethyl mercaptan with the methyl ester of azodicarboxylic acid (80). All these, of course, do not by any means exhaust the possibilities (81, 63, 57b).

It may be said that on the whole both the aliphatic and aromatic mercaptans come closer to phenols in respect to addition compound formation than to aliphatic alcohols. We are also of the opinion that the separation and study of addition types is likely to be simpler in the case of sulfur compounds than in that of oxygen compounds. As an instance we might cite the case of benzyl mercaptan adding to benzaldehyde to form benzyl α-hydroxybenzyl sulfide in the absence of a condensing agent (81), a case in which a clean cut distinction can be made between addition and condensation.

### *3. Condensations*

*With compounds containing aldehyde and ketone groups.* Numerous condensations have been reported with aldehydes (82, 78d, 74, 57j, 33), ketones (83, 82g, 78d, 77, 62a), ketonic acids (78), sugars (84, 41), aldehydes in conjunction with bases, and the like. In the synthesis of soporifics, mercaptals, formed from aldehydes, and mercaptoles, formed from ketones, have played

an important part. A very strange contrast is that the analogues of the mercaptoles cannot be made by the same procedure in the alcohol series. Mercaptals have been made from aliphatic mercaptans and dimercaptans with many aromatic aldehydes, and even cyclic aldehydes such as thienyl acetaldehyde (82g). Aromatic mercaptans have been condensed with both aliphatic and aromatic aldehydes in a wide variety of combinations. Piperonal, cinnamic aldehyde, and furfural (78d) appear in a long list of reagents, and the mercaptan proper reactions have been extended to aliphatic thio acids. The last mentioned form dithioaldehyde aliphatic acids, which show a structure analogous to that of the mercaptals. Thus, dithiobenzaldehyde acetic acid would be $(C_6H_5)CH(SCH_2COOH)_2$. Few reactions with formaldehyde have been tried (82e, 82i, 82k). Keeping in mind the complications that arise in the reaction of phenols with formaldehyde, it would be of interest to see the matter investigated. One would expect, for instance, to find the sulfur analogues of $HO(C_6H_4)CH_2(C_6H_4)OH$, and $HOC_6H_4CH_2OH$, which are formed under different conditions in the reaction of phenol and formaldehyde.

Amongst the ketones used in condensations we find acetylacetone (83a), thiophenylacetone (83), thioethylacetone (83), 2, 3-diphenylindone (77), and diketones of the type XCOYCOZ (83a) in combination with aliphatic and aromatic mercaptans, including thio acids and derived forms as, for example, $\beta$-ethoxyethyl mercaptan (83b).

$\alpha$-Ketonic acids show similar behavior readily; $\beta$-ketonic acids less readily. Thioglycolic acid condenses readily with acetoacetic ester. The data are scarce but many extensions ought to be possible (78).

Condensations with sugars are receiving a great deal of attention. Thus methyl mercaptan and grape sugar will condense to glucose methyl mercaptal, $CH_2OH(CHOH)_4CH(SCH_3)_2$. This may go over to an alkyl glucoside. Arabinose, galactose, mannose, rhamnose, xylose, lactose, rhodeose, fucose, and many others and their derivatives figure in these syntheses.

*Esterification.* Esterifications have been accomplished directly

in many cases. Thus methyl mercaptan and formic acid form a methyl trithioester. It is not imperative to use methyl formate or formamide or chloroform in the presence of alkali, though such methods are also operable. This applies to both aliphatic and aromatic types (85, 82b). Both mono- and di-acetyl compounds are reported (85c, 85d, 85e, 85f, 85g, 57k, 34, 15). Occasionally an esterification fails, as e.g. that of allyl mercaptan with formic acid, but it is because of the instability of the mercaptan (82l). An esterification with an inorganic acid, hydrochloric acid, is reported only for triphenylmethyl mercaptan, with the evolution of hydrogen sulfide (53). This would be expected by analogy. An interesting case is another such esterification of monothioethylene glycol with concentrated hydrochloric acid (19a). In this experiment the alcohol group was esterified and the mercaptan group remained unchanged. This may not be a true basis for comparing the competition between the —SH and —OH groups, since the residual groups are not the same. The analogies under more comparable conditions have been tested, the limits following in general the relations observed with alcohols, though much lower. The stability of esters decreases with increase in molecular weight (85h, 57k, 24a). The failure of mono esters to turn up in the case of formic acid is of particular interest, but it may be merely a matter of conditions. Furthermore, certain reactions of phenols which one may come across in attempts to esterify, as, for instance, with phthalic anhydride, to form either phthaleins, and $\alpha$-hydroxyanthraquinone, or the $AlCl_3$ condensation product, $HOC_6H_4COC_6H_4COOH$, have not produced their analogues as yet. The formation of $\beta$-mercaptopropyl phthalimide from $\beta$-aminopropyl mercaptan and phthalic anhydride indicates possibilities in this direction (86). It may also be noted here that reactions between some alcohols and some mercaptans to form sulfides, which are reversible, have also been considered as esterifications, i.e. the mercaptan may be treated as an acid. Thus benzyl alcohol reacts reversibly with ethyl mercaptan forming the sulfide. On the other hand, benzyl mercaptan reacts irreversibly with ethyl alcohol to form the ether (87). Thus, too, one may look upon condensations of mercaptans with aniline

to anilides (9) as another instance of esterification with the mercaptan in the rôle of an acid.

*Reimer-Tiemann types.* Condensations depending on the use of chloroform or carbon tetrachloride along with alkali have been worked out in some detail (88a). There is some analogy with alcohols and phenols. Thus mercapto acids may be made in the same way as hydroxy acids. Yet there may be some differences in orientation, and complications certainly do arise on account of ready disulfide formation from mercaptans or mercapto acids. Nor is the formation of salicylaldehyde from phenol paralleled with thiophenol, in which case an orthoformic ester is formed. The points of difference do illuminate the special problems of poor yields with oxygen compounds, pointing to explanations based on analogies to the sulfur compounds, rather than *vice versa*.

*Ester exchange.* By ester exchange we mean a condensation reaction in which substantially an esterification is accomplished by another ester (59a). This is illustrated by the equation.

$$RSH + R'ONO = RSNO + R'OH$$

Mercaptans react with organic nitrites to give a thionitrite and an alcohol or phenol (89). Even substituted mercaptans show this reaction, which we may guess is probably reversible, furnishing us directly with the oxygen analogue.

Somewhat similar are the reactions (90) characterized by the equation

$$M(SR)_2 + n\ NO \rightarrow (NO)_{n-1}MSR + NOSR$$

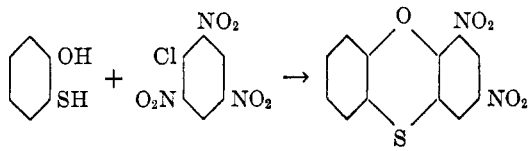
in which M = Ni, Co, or Fe. For Fe and Co, n = 3; for Ni, n = 2. Besides the esterification there is the formation of a curious metallic derivative.

*Condensations with acid chlorides and the like.* Reactions with chlorides of inorganic acids parallel the oxygen types. Yet phosphorus pentachloride, for instance, when reacting with a mercaptan may form a sulfochloride in addition to an ester (91). NOCl reacts to form thionitrites (59a). Phosgene (92), or thiophosgene (92a, 92b), and esters of chlorocarbonic acid (93)

condense normally. Polysulfide types may be obtained by the use of phosphorus sulfochloride (94), thus

$$3\ RSH + PSCl_3 \rightarrow PS(SR)_3 + 3\ HCl$$

In the case of organic acid chlorides in conjunction with alkali we have numerous analogues of the Schotten-Baumann reaction. We have illustrations from among the simplest up to the most complex mercaptans. Other than sodium salts of the mercaptans may be used. Occasionally the matter is complicated by ring closure (72), as in the case of $\beta$-mercaptoisopropyl amine forming 4-methyl-2-phenyl-thiazoline when condensation with benzoyl chloride is attempted. Oxalyl choride has been used in a number of cases (96). Picryl chloride also leads to complications due to ring closure with the reagent (85e). A peculiar case is found in the reaction with *o*-hydroxythiophenol in which "phenoxthin," or 1,3-dinitrophenothioxin, is formed (97a), thus




Further cases are too numerous to discuss (97, 85d, 82e, 82h, 74b, 59h, 57b, 57g, 50, 33, 28, 27, 14, 11, 7).

*Types related to Williamson's reaction.* The formation of sulfides analogously to ethers from organic halides and sodium mercaptides has been investigated for a large variety of compounds (98, 97c, 97e, 97n, 85c, 85d, 85e, 82c, 82g, 82h, 81b, 73, 33, 10, 9, 7, 3, 1). The reactions are not limited to sodium mercaptides. A frequent variant is found in the use of sodium ethoxide with the mercaptan and halogen derivative. It may be noted here that in some cases a complication may arise in that a sodium mercaptide will react directly with a mercaptan to form a sulfide, as seems to be the case in the reaction of cyclopentyl mercaptan and sodium ethyl mercaptide. This would lead one to expect analogies in the case of alcohols and phenols which remain to be discovered.

The halogen derivatives which may be used include chloroalkyl sulfides (97h, 82h) and sulfoxides (97h), chloroanthraquinones (97d), chlorohydrins (98x, 97n, 82c), and even chloromercaptides (98d), e.g. $C_6H_4(NO_2)SCl$. In the interesting case of condensation with $(SCN)_2$ and RS – SCN, the SCN group shows behavior analogous to that of the halogen (98b, 98t). Thus *o*-nitrophenol with NCS – SCN yields $C_6H_4(NO_2)S \cdot SCN$ with the liberation of HSCN. *β*-Naphthyl mercaptan and $C_2H_5S \cdot SCN$ yield HSCN and $(C_{10}H_7)S \cdot SC_2H_5$. These products may condense further with more mercaptan giving disulfides of higher molecular weight. Cyanogen iodide (11), somewhat analogously, will convert an –SH group to an –SCN group. On the whole, there is also no reason for not including amongst such condensations reactions with alkyl sulfates (98s, 85d, 85e, 73, 10), with sulfonic acids and esters (100e, 98r, 98v, 97c, 81b, 15) and with rarer reagents, such as benzyl nitrate (98p). All of these have been tried to some extent.

*Reactions with aryldiazonium salts, etc.* Attempts have been made to parallel the action of phenols on diazonium compounds to form azo compounds. Aromatic mercaptans react with diazonium compounds to form diazothiophenol ethers which are converted readily to sulfides (99, 87). Disulfides are found as by-products and, in the not unusual contingency of an explosion, as the main products. There is a distinct contrast in these observations which deserves a great deal more attention.

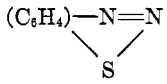
*Reactions with chloro acids, etc.* Sulfide formation is the essential background of condensations with chloro acids, which resemble those given above for other chlorine-containing compounds (100, 98c, 97, 97j, 97k, 85e, 82j, 59h, 3). Esters of the chloro acids apparently do as well (100d, 93). To complete our list we would mention chloro- and bromo-ketones and an instance where diiododiethyl sulfone reacted analogously. Of more interest are the deviations from these standard forms, such as, for example, the reaction of benzyl mercaptan with ethylene dichloride and alcoholic alkali. Surprisingly, the *unsaturated* BzSCH =CHSBz is formed, as if there were a momentary formation of acetylene (98c). Curious also is the inversion that may occur with par-

ticular mercaptans possessing unusual characteristics. An instance arises in the condensation of β-aminoethyl mercaptan with ethylene chlorohydrin in which the hydroxyl group, rather than the chlorine atom, reacts with the hydrogen of the −SH group forming $NH_2CH_2CH_2S \cdot CH_2 \cdot CH_2Cl$. In all other cases observed chlorohydrin reacts by way of the chlorine atom.

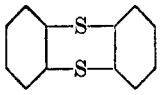
That sodium bisulfite may be split out in a condensation is illustrated by the combination of sodium anthraquinone sulfonates with mercaptans in the presence of alkali to form alkylmercaptoanthraquinones (100e, 100g). An entirely similar splitting out of $KNO_2$ occurs when nitroanthraquinone is treated with a potassium mercaptide (100f). We know of no analogous reactions in the oxygen series.

*Ring closures.* Several examples exist of aromatic mercaptans which on treatment with alkali form heterocyclic compounds (101, 97a, 86, 72, 57k, 27, 9). Such is *o*-(γ-chloropropyl)-thiophenol which forms αβ-benzopentamethylene sulfide or "thiochroman" (101d).

Otherwise one may rely on more or less standard procedures. Thio amides and ethylene dibromide (101a, 101b, 72) dithioethylene glycol and benzal chloride or ethylene dibromide (101e, 9), will yield ring structures. *o*-Aminophenyl mercaptans and nitrous acid go to diazo sulfides (101),



In this group we may also place the conversion of phenyl mercaptan to thianthrene



in the presence of aluminium chloride (101c). Again analogy proves to be a safe guide.

### *4. Oxidations*

*Oxidations by concentrated sulfuric acid, nitric acid, and the like.* That the first step in the oxidation of mercaptans is disulfide formation and the last step sulfonic acid formation is well known. Yet the probable existence of sulfoxides and sulfones as intermediate products is quite usually ignored. Concentrated sulfuric acid and even sulfur trioxide are reported to form disulfides only (97e, 59, 5), yet evidence is available that other products are also present, e.g. phenyl mercaptan yields thianthrene and possibly diphenylene-*p*-disulfide and compounds responsible for a blue color (103). There is hardly any doubt that there is further action beyond simple disulfide formation, characterized by ring closures and polymerization (103, 101c). Our own work clearly indicates a similar situation for aliphatic types as well. In fact, it is possible to obtain parallel results with aluminium chloride, zinc chloride or phosphorus pentoxide once disulfide formation sets in (101c). It is also possible to take the stand that esterification of the mercaptans by the sulfuric acid precedes the oxidation proper to disulfides, the ester formed breaking up into a disulfide and sulfur dioxide (59j), i.e.

$$(RS)_2SO_2 \longrightarrow R_2S_2 + SO_2$$

Another postulate calls for the formation of thiosulfonic esters, $RSO_2SR$ (24b). Still another angle in oxidations with sulfuric acid is revealed in what seems to be trisulfide formation from free sulfur originating from hydrogen sulfide and sulfur dioxide liberated, a reaction surmised to be

$$2\,RSH + 2\,S \longrightarrow R_2S_3 + H_2S$$

The trisulfides are credited with responsibility for the corrosiveness of naphthas (104).

Oxidations with nitric acid, though frequent, have not been studied in detail (109, 105, 98a, 51, 32, 29). Thus the possibility of nitration seems to have been largely overlooked, except in a case in which fuming nitric acid has been used on 2,4-di(methylmercapto)-1-ethylbenzene to produce the monosulfoxide of 5-nitro-2,4-di(methylmercapto)-1-ethylbenzene (85e). Again, as in the

case of urea types functioning like mercaptans, the presence of nitrous acid along with the nitric acid would make quite a difference (81a). In dealing with arylimidazole mercaptans, nitric acid is responsible for the removal of the —SH group altogether (106, 73). This reminds one of the same phenomenon when chromic acid is used jointly with sulfuric acid (107, 106). The combination of nitric and sulfuric acids yields polymers in addition to sulfonic acids (15), and there is no telling what aqua regia and the like may do. Mixtures of nitrogen oxides may be mild enough to yield sulfoxy compounds in some cases (98f, 98o), whereas nitrosyl chloride has been used gently to make disulfides (108, 96). But we have learned already that the latter also makes thionitrites (RSNO), which may be intermediates. One would also expect sulfuryl chloride to behave similarly if used mildly. More definite results may be expected with permanganate (109, 106, 91) and especially hydrogen peroxide (110, 85b, 16b), but very little has been done along those lines.

*Disulfide formation in oxidation.* If disulfide formation is an objective, one may even use copper sulfate (111, 23) or lead peroxide (98f, 15). Phosphorus oxychloride (112, 97b, 96), tellurium tetrachloride (113), etc., may function to some extent as oxidizing agents, and ferric chloride and ferricyanides serve the same purpose (114, 107, 97l, 97n, 53, 19a, 11, 10). This reveals a wide scope for inorganic oxidizing agents, quite a few of which have been made the subject of patents, since the odors of disulfides are not as objectionable in naphthas as are those of mercaptans.

Air is quite adequate in the production of disulfides from mercaptans (115, 98h, 5, 74a, 62, 62a, 57i, 57k, 52, 50, 33, 19, 3). It is difficult to keep solutions of mercaptans in oil from oxidizing. This is particularly marked under alkaline conditions. On the whole, very little has been done in this field. When we consider that cysteine is oxidized to cystine by oxygen under biological conditions (74a) or in the presence or iron salts (114), and that there are other balances of the same type in the body, one might wish that much more had been done in this field.

The place of oxygen in disulfide formation can be taken by

ozone (116) or by electrolytic generation of oxygen (117, 62). The most famous equivalent, however, is sulfur (118). The well-known "doctor sweetening" of oils consists of converting mercaptans to lead mercaptides by reaction with alkaline plumbite solution. These are converted by free sulfur to disulfides and lead sulfide. Recently it has been shown that basic mercaptides are formed, and even peroxide derivatives, but that the final effect due to the addition of sulfur is either a slow or a rapid conversion to disulfides. We might suggest that biochemical research on similar reactions of compounds containing an —SH group involving oxygen may draw some inspiration from the work with sulfur. Reaction of mercaptans with sulfur has yielded disulfides.

*Oxidations by halogens and halogen compounds.* When we come to oxidations with halogens careful distinctions have to be made. Iodine seems to be the only one that can be relied on to yield disulfides only under alkaline conditions (119, 107, 106, 97g, 3). Bromine (120, 117, 97l, 85c, 78b, 59h, 57j, 48s, 31, 19a, 15, 5) and chlorine (121, 120c, 98h, 98s, 97m, 57j, 53, 15) are likely to yield sulfobromides and sulfochlorides under acid conditions and may lead to sulfoxides, sulfones and even sulfonic acids under alkaline conditions. In the case of some complex mercaptans which are very easily oxidized we are not certain that even iodine may not lead to sulfonic acid formation, and bromine has been known to split off the —SH group altogether when in excess, e.g. 1,4-acetamidonaphthyl mercaptan forms 4-bromo-1-acetylnaphthylamine (57j). Easily oxidized mercaptans, as *p*-phenylene dimercaptan, form polymeric disulfides first and substituted polymers subsequently (15). Commercial application has been made of this type of oxidation to "sweetening," or conversion to disulfides, by means of sodium hypochlorite solutions (121, 59j). This indicates that close control of conditions will segregate the various types of possible products, and where mixtures have been obtained consistency may yet be introduced.

Halogen-containing compounds such as sulfurylchloride (122, 120, 98o, 96, 53), thionyl chloride (123, 118a, 96), the sulfur chlorides (124, 123a, 118a, 92a), and even chloropicrin (125) exert an

oxidizing action in a variety of ways. The sulfur chlorides yield polysulfides, which are described as "not sweet" products. Tri-, tetra-, and penta-sulfides are on record. A distinction has been made between mercaptans on the basis of their reactions with sulfur monochloride (124c). A "real" mercaptan is one that reacts without liberation of sulfur; a "potential" mercaptan is one that reacts with liberation of sulfur. The distinction is illustrated thus:

$$2\ CH_3CH_2SK + S_2Cl_2 \rightarrow (CH_3CH)_2S{=}S + 2\ KCl \text{ (real mercaptan)}$$

$$2\ (C_6H_5)C(=NH)(SK) + S_2Cl_2 \rightarrow S(C_6H_5C : NH)_2 + 2\ KCl + 3\ S$$

At the same time, it seems that if sufficiently diluted the monochloride may yield the disulfide. Thionyl chloride has been used for polysulfide formation. Sulfuryl chloride, however, yields disulfides mixed with sulfochlorides. In this instance, the sulfochlorides probably condense with mercaptan to form the disulfides:

$$RSH + R'SCl \rightarrow RS \cdot SR'$$

Chloropicrin normally produces disulfides, but it may also form compounds of the general formula $(RS)_3COR\ (SR)_3$ through loss of nitrous acid in the course of such oxidations.

*Miscellaneous oxidations.* Miscellaneous oxidation reactions abound. At times there are ring closures in complex cases (125a). We find diazobenzene chloride leading to disulfide formation (99). So may hydroxylamine (120), aryliminomethylenesulfoxylic acids (126), sulfinic acids (102b, 31), disulfoxides (123a, 31), formaldehyde sulfoxylate (126, 2) and chlorosulfonic acid (127, 59). This means that mercaptans are good reducing agents. They reduce, as a further instance, quinone to hydroquinone forming probably thio aldehydes (128). Even sulfur dioxide may act as an oxidizing agent with reference to mercaptans. In the presence of hydrogen chloride, sulfur dioxide may be used to make disulfides and even trisulfides (129, 123a). Polysulfide formation by oxidation with what we are accustomed not to consider as oxidizing agents may also be obtained with thionyl aniline, $(C_6H_5NSO)$, and diethylaniline sulfide (130).

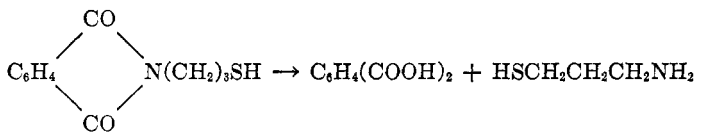
Many interesting problems arise in this field. When we note sporadic observations such as the formation of hydrogen peroxide in the autoxidation of mercaptans and the formation of peroxides by mercaptides (131), we feel that only a beginning has been made in the study of the oxidation of mercaptans. Even though we have but little as yet upon which to found analogies with phenols and alcohols, the possibility is being opened up (132, 130, 118d, 117, 98e, 30a, 28).

### *5. Miscellaneous reactions*

Mercaptans react with alkyl magnesium halides to produce alkylmercapto magnesium halides and hydrocarbons (133). This is in line with the analogous behavior of alcohols in Grignard condensations. Ethyl mercaptan, ethyl magnesium bromide and benzoyl chloride yield ethyl thiobenzoate; if ethyl chloroformate is used, ethyl thiocarbonate is obtained (133a). Synthetic building up of mercaptans may be accomplished as in the case of alcohols.

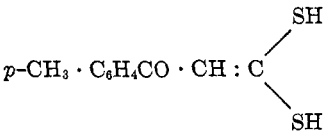
Substitution of —SH hydrogen together with substitution in the ring takes place when aromatic mercaptans are treated with chlorine in chloroform or carbon tetrachloride (120c, 98h, 34). There may be simultaneous oxidation to halogen-substituted disulfides. We have already remarked that excess halogen may cause the entire loss of the —SH group in complex mercaptans (98h). Somewhat puzzling then, is the reported formation of ethyl bromide from ethyl mercaptan and bromine (19b). It is quite to be expected however, in the case of the curious mercaptosilicon chloride, $SiCl_3SH$, which gives $SiCl_3Br$ (196).

A "Gabriel" reaction (134, 120a, 101b), amounting to the conversion of one mercaptan to another, is illustrated by the case of the reaction of *N*-($\gamma$-mercaptopropyl)-phthalimide with fuming HCl in a bomb tube:



Mercaptoamines are thus formed. This parallels aminoalcohol formation.

Stress should be laid on the observed substitution of —SH groups, not only because of the apparent analogy with alcohol chemistry, but also because of the similarity to reactions in which an —SH group is hydrolyzed off, as it were, with the formation of hydrogen sulfide (135, 120c, 57, 53, 9, 3). Thus the same $SiCl_3SH$ on treatment with alcohol yields hydrogen sulfide (19b), while triphenylmethyl mercaptan loses hydrogen sulfide on treatment with cold concentrated sulfuric acid, boiling acetic anhydride, dilute alkali, sodium ethoxide or even alcoholic silver nitrate (53). The last reaction shows an analogy with alkali hydrosulfides, since silver sulfide is formed. Removal of —SH groups by similar mechanisms is possible with alcoholic ammonia or potassium hydroxide at elevated temperatures in some exceptional types, as, for example,




(9)

Simple hydrolysis with water alone at elevated temperatures has also been reported, at least for ethyl mercaptan.

A claim has been made that mercaptides react with disulfides (97f) in a kind of rearrangement:

$$R'SSR' + 2\ R''SK \rightarrow 2\ R'SK + R''SSR'$$

Such shifts may not be uncommon. Another phenomenon which has received practically no attention is the possible polymerization of mercaptans (74b).

A rather unusual reaction, too, is the reduction of substituted persulfides (RSSH) to simpler mercaptans (RSH) by sodium arsenite or potassium cyanide (136).

A large variety of analogies may be suggested for research. These would be parallel to pinacoline transformations, such as the transformation of di-primary, primary-secondary, primary-tertiary and di-tertiary dimercaptans to thio ketones. One might

parallel the dehydration of aromatic alcohols mixed with aromatic hydrocarbons, e.g. the reaction of benzyl mercaptan and benzene in the presence of sulfuric and acetic acids to form diphenylmethane, or the similar reaction to synthesize triphenylmethane. There should be analogues of the condensations with the "methane carbon atom," such as that of phenol, oxalic and sulfuric acids to form aurin $(HOC_6H_4)_2C{=}C_6H_4{=}0$. Condensations of anthrol derivatives suggest numerous possibilities in the dye field. Some of the simpler reactions need investigation, as, for instance, the formation of the analogue of resorcin green, which is formed by the action of nitrous acid on resorcinol, or the formation of dinaphthols by the action of ferric chloride on the naphthols. One may expect a material increase of our knowledge contributory to analytical detection and to practical utilization.

To augment our list of reactions, untouched or practically untouched, we may mention possibilities that suggest themselves in the reduction of phenol to hexahydrophenol, oxidation of side chains of phenols, reduction of hydroxy acids by hydrogen iodide, direct replacement of groups, as Cl or $-NH_2$, by $-OH$, Skraup's synthesis, Kolbe and Schmitt syntheses, and syntheses of hydroxy acids, as illustrative of a host of not only analogies, but also contrasts.

## III. METHODS OF PREPARATION AND PURIFICATION

### *1. Occurrence and isolation from natural products*

Methyl mercaptan has been reported in numerous biological sources, in fresh roots as well as in decomposing organic matter (137). Ethyl and isoamyl mercaptans seem to be normal by-products in the metabolism of yeast or micro-organisms (138). The reason why other homologues have not been reported lies probably in the qualitative way in which the matter has been approached. If we include thio acids, sulfur-containing amino acids as cysteine, glutathione, in our list, the $-SH$ group becomes almost omnipresent (139). Coagulated egg white gives the nitroprusside test (139c). A thio sugar of known constitution has been found in yeast. It is even stated that insulin's physiological

activity depends on the sulfur part of the molecule. If we consider the multiplicity of reactions possible in the decomposition of these more complex compounds containing —SH groups and the patent fact that simpler mercaptans do form readily in the metabolism of such foods as asparagus or spinach (137b, 137c), it is not surprising that petroleum, its distillates, shale oils and coal tar distillates are good sources of mercaptans, since they ultimately originate from living matter.

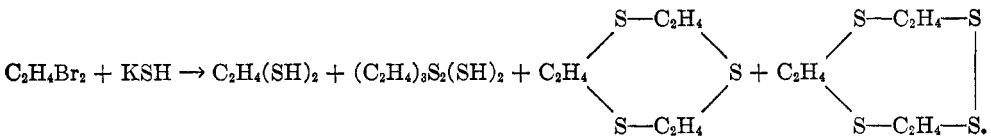
The isolation of mercaptans from natural sources, if it be merely a matter of scientific interest, can be accomplished by a judicious choice of reactions. Industrially, aqueous caustic soda is employed to remove the lower aliphatic mercaptans and some thiophenol, and hence these washings may serve as a limited source of of these mercaptans. Mercaptans can also be recovered from refinery acid sludges in which they dissolve as such, especially at lower temperatures. Quantitative separations in the form of mercury derivatives and the like, are, of course, possible, even if they are not practised.

### *2. Synthetic methods*

*Direct introduction of —SH group by substitution.* The most obvious approach in the synthesis of mercaptans is the substitution of an inorganic radical already present in an organic compound by an —SH group from an inorganic source, such as hydrogen sulfide, a sulfide, or a hydrosulfide. The simplest case reported recently is the formation of ethyl mercaptan from ethyl iodide and aqueous hydrogen sulfide (140). This takes place even in acid solution and is accelerated by the presence of precipitated sulfides or other adsorbing agents. Rather unexpected is the reaction of hydrogen sulfide with silicon tetrachloride leading to the formation of $SiCl_3SH$ (19b). Apparently one might expect analogies to appear in the inorganic field as well.

Reactions with hydrosulfides have been practised on the most varied types of halogenated compounds even to the extent of determining the orientation of entering —SH groups (141, 132a, 114b, 105f, 98u, 78b, 74b, 57d, 53, 51, 29, 27, 19). Thio acids

(141p, 119e, 119f, 111, 57i), thio sugars (141c, 141r, 141s, 141t), thiopurine derivatives and the like (141b, 141e, 141m, 110b, 98l, 98q, 57g, 33), have been made by such procedures. We should like to point out that it is often overlooked that there may be other products formed, as, for instance, dithio acids in the thio acid syntheses. It is also possible to get polysulfides, as, for instance, triethylene disulfide dimercaptan and more complex compounds in the reaction of ethylene bromide with KSH (115d), thus




*Variants on direct use of hydrosulfide.* The conditions are often varied, sodium sulfide being used instead of the hydrosulfide; nor is it necessary to work with a halogen derivative (142, 141g). Thus, analogously to the potash fusion of sodium benzenesulfonate to obtain phenol, one may get a small yield of thiophenol by the use of potassium hydrosulfide. A general method has been reported whereby alcohols are treated with red phosphorus, moist sodium sulfate and sodium sulfide, and bromine (143). This is essentially a modification of the above procedures, with the curious fact that the sodium sulfate is a source of sodium sulfide or hydrogen sulfide:

$$6\ ROH + 3\ Br_2 + 2\ P \rightarrow 6\ RBr + 2\ P(OH)_3$$

$$4\ P(OH)_3 + Na_2SO_4 \rightarrow Na_2S + 4\ H_3PO_4$$

$$Na_2S + H_3PO_4 \rightarrow Na_2HPO_4 + H_2S$$

$$RBr + H_2S \rightarrow RSH + HBr$$

The yields are good.

In the same class we may put reactions whereby an $-NH_2$ group is replaced by —SH by diazotizing and treating with an alcoholic sulfide or hydrosulfide to liberate nitrogen. Better yields are obtained if the diazotized compound is first treated with a xanthate or a thiosulfate and then hydrolyzed. In some cases the use of xanthates to react with the halogen derivative

can be made direct. On hydrolysis the mercaptan structure is opened up (144, 141k, 98s, 92a, 8).

*Addition of hydrogen sulfide to unsaturated compounds, and reactions with alcohols and the like.* Before we go on with cases of this sort we stop to consider the cases in which hydrogen sulfide has been used to add to unsaturated compounds. Strangely enough, direct addition to olefins has not been investigated, although ethyl mercaptan is mentioned as a by-product in the reaction of acetylene with hydrogen sulfide at 425–50° (145). Indirectly this is accomplished when alcohols are passed over thorium dioxide with hydrogen sulfide at temperatures at which olefins may form (146, 58). There is also reason to believe that alcohols may be sufficiently dehydrated by concentrated sulfuric acid to react with hydrogen sulfide to form mercaptans, at least of the aliphatic series (41). In the case of sugars the —SH group may be introduced by means of hydrogen sulfide in the presence of pyridine (141i, 141s, 84, 42). Furthermore, esters may be simultaneously hydrolyzed and caused to react with hydrogen sulfide to form mercaptans (87). A very interesting case of a more complex nature is the conversion of the corresponding —OH compounds to the carbothiols of malachite green and of crystal violet merely by the action of hydrogen sulfide (13a). We also think it proper to surmise that the formation of mercaptans in fermentation may be due to the reaction of alcohols with hydrogen sulfide. It may not be safe to speculate that wherever water adds to yield hydroxy compounds, hydrogen sulfide will add to yield mercaptans, yet we can cite cases in which such similarities are well indicated. Benzalacetophenone will add hydrogen sulfide to form a sulfhydrin (147); with favorable structures a —C=N— group will add hydrogen sulfide to form a mercapto compound (125a), and the like.

It is but a small transition from the above to cases where phosphorus sulfides have been made to react with hydroxy compounds (148), such as phenols (141m, 132b), carbostyril (16b), hydroxyquinaldine (16b), and benzohydrol (148a), to form the corresponding thiols. Aluminium sulfide and hydrated sodium sulfate (57) constitute a reagent somewhat analogous to that

acting in the instances in which hydrogen sulfide reacts as it is formed.

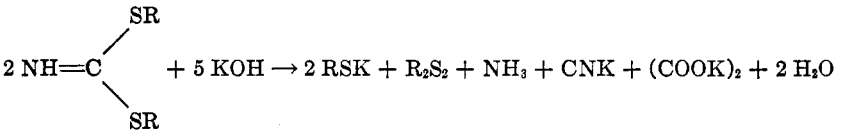
*By various hydrolyses.* Very numerous are the cases in which the mercaptans are obtained finally by the hydrolysis of some compound which may itself be a synthetic mercaptan. We have mentioned the Gabriel reaction for aminomercaptans, but it need not be restricted to this type and is applicable to the formation of dimercaptans (134, 120a, 101b, 86, 72, 3). Xanthates and xanthic acids can be hydrolyzed to mercaptans or mercapto acids (149, 144, 144a, 144b, 144c, 141f, 119f, 98s, 93, 8). Hydrolysis of mercapturic acids gives cysteins (137g, 74a). Hydrolysis of cystine derivatives yields mercaptans (150). Many thioglycols have been made by the hydrolysis of thiourethans (14). Thus,

$$NH_2 \cdot CS \cdot S(CH_2)_nS \cdot C : S \cdot NH_2 + 4\ KOH \rightarrow 2\ KSCN + KS(CH_2)_nSK.$$

Ring closures may occur (151, 120a, 106, 97g, 12, 10), such as when acetylallylarylthioureas on refluxing with dilute hydrochloric acid yield arylimidazole mercaptans (73). Rings are opened up also, as when diphenylthiohydantoin yields on hydrolysis thioglycolic acid (152).

Hydrolysis of $\beta$-ethylmercapto-crotonic acid ethyl ester favors preferentially the splitting off of a mercaptan (100a). In the case of a compound like $C_6H_4(NO_2)(CHSCONH_2)$ (156), hydrolysis leads to the formation of a mercaptan. We may mention as sources of mercaptans such compounds as $CCl_3—C(SCH_3)(NH \cdot HCl)$ (76), mercaptotriarylcarbonium salts (153), esters of thio acids (96), the addition compound of dimethyl sulfate with thiourea (154), and thiourea derivatives (154a, 107, 21a), phenylthiomethyl acetate (98f), phenylsulfoxyacetic acid (155), thio esters of thiophthalic acid (141o), the diacetone compound of 3-thioglucose and the like (158, 141c, 141s, 141t, 132j, 84a), thiourethan glycoside (14), mercaptals (84), ethyl trithiocarbonic acid (144), and types like $(C_6H_5S)_2C(CH_3)(CH_2COOC_2H_5)$ (78). Add to this heterogeneous group the hydrolysis of Grignard reagents containing sulfur, usually made by the use of free sulfur, to obtain quite a variety of mercaptans (157, 141, 133, 117,

30, 30a, 25). A very general equation, representing hydrolysis of thiosulfocarbamates (6), is expressed by



and still another involving thio acid esters (6):

$$NH_4CS \cdot SR \rightarrow NCSH + HSR$$

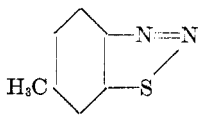
Rather unusual are conversions of thiocyanates to mercaptans by concentrated sulfuric acid (159,1). Dimethyl sulfate in very exceptional cases can be made to remove an —SH group from a compound to form methyl mercaptan (125a). The group $-SCOC_6H_5$ can be converted to an —SH group by ordinary hydrolysis when appearing in ring compounds (156).

There remain also a few cases where drastic action which may be considered as hydrolysis leads to mercaptan formation. Such is the formation of *o*-thiocresol from thionaphthene (160) and the decomposition of disulfides to mercaptans and sulfonic acids along with other products by caustic potash (161, 124e, 102b). More complex variants will not be discussed here (162).

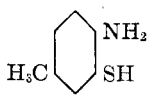
*By reductions.* Quite as important are numerous cases in which mercaptans have been synthesized by reducing some other compound. The disulfides, if available, are very convenient (163, 146b, 138d, 117, 114b, 101, 97, 97m, 82j, 57m, 9c, 8c, 6). As reducing agents we find alkali sulfides (136, 132i, 124e, 100b, 31, 19a), glucose in alkali (163, 97n, 82b), zinc dust in alkali or acid (161b, 123a, 115b, 98r, 97j, 35, 15), active aluminium (163a, 163i), sodium (163d, 97i, 97j, 82h), tin and acid (82b), electrolysis at the cathode (114a), the Grignard reagent (30), mercury with or without chloroform (163b), and mercaptides themselves (97f). It is doubtful whether sulfides as a class are reducible by such means to mercaptans, yet exceptions seem to exist in the case of *o*-nitrophenyl sulfide and sulfides of the type $C_6H_5CH_2$—$SCH_2COR$ (164). In the latter cases benzyl mercaptan has been obtained by reduction with sodium, zinc and acid, and even hy-

droxylamine hydrochloride (97j). We are not prepared to say whether these are really exceptions, since the field has not been widely investigated. The reduction of tri- and tetra-sulfides to mercaptans, which takes place with the same reagents as the disulfides, is more easily understood (123a, 82h).

Other compounds that are reducible to mercaptans are sulfonic acids (165, 121a), thiosulfonic acids and their esters (165, 161c), and sulfochlorides derived from sulfonic acids (166, 157b, 119c, 115, 114c, 102c, 100, 100c, 98e, 98h, 97, 97e, 85c, 85d, 85e, 67, 59i, 57j, 57k, 34, 32, 11) either under acid conditions with metals or by electrolysis (167, 117, 115c, 114a). Sulfonamides may be reduced by hydrogen iodide and phosphorus (168). This list may be expanded to include sulfoxides (169, 161c, 115b, 105b, 99a, 31), sulfinic acids (170, 119c, 115b, 82g, 16) and sulfenic acids (171) and their derivatives, alkyl hyposulfites (172, 132e) and thiocyanates (159a, 100g, 19), sulfoxylates (2) and sulfanilides (167b). Of some special interest is the reduction by aniline of compounds of the type $RSCCl_3$, where R is an aromatic radical, to mercaptans of the aromatic series with the formation of triphenylguanidine as a by-product (173, 132g). Little explored has been the reduction of ring compounds containing sulfur to mercaptans. Thus from a knowledge that thionaphthene is reducible to *o*-ethylthiophenol (174), or that toluylene diazosulfide




is reducible to 1-methyl-4-amino-3-mercaptobenzene (175)




we can visualize many possibilities of the similar opening up of sulfur-containing rings.

*By reaction with sulfur.* Reaction with sulfur may serve as a means of forming mercaptans. Sulfur reacts with benzene in the

presence of aluminium chloride to form phenyl mercaptan (176, 118e). It reacts similarly with phenylhydrazine (177), diphenylamine (178), and aminodiphenylamine (178). The reaction of sulfur with hydrocarbons unquestionably yields mercaptans, but the matter has been taken up only very qualitatively, and, to judge from the number of cases in which they have not even been looked for, rather carelessly.

*By thermal or similar decomposition.* A few instances are available in which thermal or similar decomposition by scission serves as a source of mercaptans. These might have a very important bearing on the frequently observed evolution of hydrogen sulfide and mercaptan formation on heating crude petroleum or its fractions whether they have been refined or not. Mercaptides, sulfides and disulfides are definite sources of mercaptans (179, 124d, 98c, 77, 57c, 57f, 32a, 7). Sulfonic and thiosulfonic acids and their derivatives, sulfoxides, sulfocyanacetic esters, and iminothiocarbonic esters, $(RS)_2C{:}NH$, have also been mentioned (182, 162f, 162h, 155, 115a, 78, 59f, 6).. In a theoretical fashion derivatives of thiourea and xanthates have been studied (180, 162e, 151c, 149, 81a, 28, 6). Observations of mercaptan evolution have been made occasionally in attempts to distill complex sulfur compounds (181, 148c, 128a, 97l, 77). In these cases there seems to have been established a definite tendency for alkylmercapto groups to be split off on heating as component parts of simple mercaptans provided a hydrogen atom is available. Simple fundamental investigations are conspicuously absent.

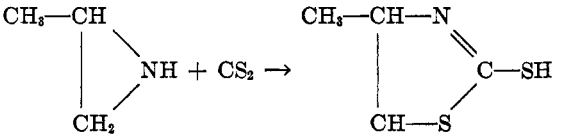
*By condensation.* Condensations may be called upon in mercaptan syntheses. An interesting type is represented in the formation of phenyl $\beta,\beta$-dimercaptovinyl ketone from acetophenone and carbon disulfide (97c, 9), thus

$$C_6H_5COCH_3 + CS_2 + 2\ KOH \rightarrow C_6H_5COCH{=}CS + K_2S + 2\ H_2O$$

$$C_6H_5COCH : CS + K_2S \rightarrow C_6H_5COCH{=}C(SK)_2$$

Similar condensations are possible with acetone dicarbonic acid ester, hydroxyquinoline derivatives (183), sulfocarbazinic acids ($RNH{\cdot}NH{\cdot}CS{\cdot}SH$) (57a), ketones like $\alpha$-thienyl methyl ke-

tone (9). Xanthates may be used in these reactions, which serve also as a basis for synthesizing mercaptothiazolines. Thiurets and alkyl iodide addition compounds of urea with primary and secondary amines furnish mercaptans (184). We find a few instances of direct condensation with carbon disulfide. Thus, potassium azide reacts to form potassium azidodithiocarbamate, $KS \cdot C(:S) \cdot N_3$, which has a mercaptan structure (57e). The general reaction $RHgOH + CS_2 \rightarrow RHgSH + COS$ has also been noted (180a). The substances RHgSH may be considered as mercaptans. Mercaptothiazoline formation (151b, 120a, 97g) may also be illustrated simply for the case of 4-methyl-2-mercaptothiazoline from propylenimine, thus



Ring closure, too, is thus illustrated (151, 151a, 151b, 151d, 151e, 106, 97g, 10). More attention, too, should be paid to the relatively easily carried out reaction between hydrogen sulfide and formaldehyde (185) which is said to result in the interesting stable substance, methylene mercaptan, $CH_2(SH)_2$. This is in striking contrast with the instability of two —OH groups on the same carbon atom. On the other hand, we may remark here, all efforts to make $NH_2SH$ have failed (186). Amongst the curiosities are also the "thioprussiamic acids" (187), obtained by the reaction of thiourea with ammonium thiocyanate, for example,

$$(NH_2)_2 : (CN)_3 \cdot NH \cdot (CN)_3 (NH_2) (SH)$$

Another type which is receiving a little attention is that represented by the formula RCSSH, dithio acids or carbithionic acids (161a, 136). They may be made from aldehydes and hydrogen persulfide directly (141q), e.g.

$$C_6H_5CHO + H_2S_2 \rightarrow C_6H_5CSSH + H_2O$$

and are stronger acids, as a rule, than acetic acid. Alternative approaches are to be found in the production of dithioformic

acid from chloroform and potassium sulfide (141p), or the formation of $C_2H_5SSH$ by reducing sodium ethyl thiosulfate with potassium sulfide (136). These dithio acids may serve as sources of simple mercaptans, since they may be reduced by such reagents as potassium cyanide or sodium arsenite (136).

It is apparent that the scope of synthetic methods may be expanded a great deal by paying closer heed to suggestions from oxygen chemistry. Analogies should be attempted, for instance, to aldol condensations and the Cannizzaro reaction, and to various means employed for reducing aldehydes, ketones, and quinones to alcohols, glycols and phenols. Thio aldehydes should add hydrogen cyanide, and then become convertible to thio acids. To mention but a few prospects, it should be possible to prepare mercaptocitric acid, to parallel the closure of phenylisocrotonic acid to $\alpha$-naphthol, to prepare thiopinacones, or to obtain exact analogies of the two types of hydrolysis of acetoacetic ester. But, perhaps, most important of all would be a re-examination of the old data with a view toward making them more valuable from both the practical and the scientific viewpoints.

## IV. DETECTION AND DETERMINATION

A few color tests are described, none of which, however, has been elaborated. The reaction of nitrosylmercaptides with nascent nitrous acid is said to distinguish primary and secondary aliphatic mercaptans by the formation of a red color (188). Tertiary and aromatic mercaptans as well as thio acids give a green color turning to red. For triphenylmethyl mercaptan a sensitivity of 1:7500 is given. Ethyl nitrite or $N_2O_4$ also give red colors (189). Chloropicrin, bromopicrin and tetranitromethane (190) have been used to distinguish between ethyl mercaptan and ethyl sulfide, but not too successfully. There is also much to be desired in the study of color changes on the addition of concentrated sulfuric acid (150, 9). All we can say is that they are many,—the usual gamut being from green to blue. A similar situation exists with tests with ferric salts (191, 141h, 141j, 119f). Mercaptans proper and thio acids should yield deep reds, yet $\alpha$-mercaptocinnamic acid gives a deep green (191).

Identification by derivatives has fared considerably better. Many mercaptides (192, 102a) have been described, as well as mercaptals, mercaptoles (192h), and the like. 3-Nitrophthalic anhydride has been strongly recommended for this purpose (193).

Some efforts have been made to develop alkalimetric titration of aliphatic mercapto acids (194). If one has favorable conditions there are available titration methods with iodine and alkali (195, 44a), permanganate (52), or silver nitrate with ammonium thiocyanate (196). If only mercaptans are present, lamp sulfur determination may be made if no great accuracy is required (57n). A method not sufficiently well-known is one based on the reaction of a mercaptan with methyl magnesium iodide (197). Methane is formed and its volume is measured:

$$RSH + CH_3MgI \rightarrow CH_4 + RSMgI$$

The chief weakness of all the methods reported here is that they require particularly suitable conditions for their execution, and that they have not been tried on a sufficient variety of mercaptans.

We may add for completeness that it is possible that mercaptans may be of use as analytical reagents. A hint to that effect is to be found in the fact that thioacetamide may be used as a reagent for arsonic acids (198). From a knowledge of the characteristics of mercaptals and mercaptoles, mercaptans may serve as reagents for detecting and determining aldehydes and ketones (192h). In fact many reactions of mercaptans may be so adapted.

## V. SPECIAL INTERESTS ATTACHING TO MERCAPTANS

We have mentioned the special interest that attaches to the study of the behavior of the —SH group in biological chemistry. The physiological effects, which may be serious, have been amply described (199). Severe irritations may occur from contact with liquid mercaptans, whereas vapors cause giddiness and headache. A remarkable effect on the eyes is the involuntary drooping of the lids accompanied by a protracted sensitivity to light. And yet mercaptans have been reported in the skin itself! Metabolic experiments are being multiplied, but the acme of interest lies in the regulative action in cell metabolism of compounds con-

taining mercapto groups, particularly reduced glutathione, cysteine and thioglycolic acid, when present in equilibrium with the disulfide forms (200, 137d). Additive compounds of the two forms have been postulated, peroxide formation has been asserted and denied, and the nature of the oxidations that go on has been studied from the point of view of autocatalysis. We cannot review the mass of data which is being accumulated, mostly because of its chaotic condition, but we would point out that the —SH group has been involved in discussions of topics from the fertilization by spermatazoa to the cure of cancer.

An outgrowth of such interest is the application of mercapto compounds to therapeutic uses (201) and even to synthetic food problems (202, 163h). Amino metal mercapto compounds, such as the sodium salt of 4-acetylamino-2-argentomercaptobenzene-1-carboxylic acid, are useful in spirochete infections. Metal mercapto acid esters are also used. The addition compound of $\alpha$-furfuryl mercaptan with the Grignard reagent has been used to synthesize derivatives showing vesicant action (35). We have already mentioned the well-known syntheses of soporifics from mercaptals and mercaptoles. Therapeutic use has been made also of the metallic compounds of thioglucose (203). Quite engaging, too, is the discovery that furfuryl mercaptan and $\alpha$-hydroxymethylfurfuryl mercaptan and their disulfides make a synthetic coffee aroma (202).

In synthetic work a varied use of mercaptans may be found. Optically active amyl mercaptan has been used for racemic splitting of sugars (204). The greatest use of mercaptans, of course, has been as intermediates in the synthesis of dyes, particularly vat dyes. Thus, the anthraquinone series has been pretty well covered and thioindigos are derived from thio acids (205). Amino thiophenol serves as the starting point for indamine colors (206). Of some importance is the observation of the bathochromic action of the methylmercapto group in azo dyes (206). To deepen shades it is, therefore, often desirable to obtain a mercaptan and methylate it. The rubber field as well claims efforts in the direction of synthetic mercapto compounds (207). The mercaptobenzothiazoles stand out in importance, but it is highly probable that others will be found.

A vast field for the production and conversion of mercaptans is to be found in petroleum technology. If all the mercaptans present in unrefined naphthas in this country were to be recovered there would be available, conservatively, from 150 to 200 tons of mercaptans per day. Many a process could be evolved for their utilization if more attention were paid to the fundamental chemistry of at least the relatively simpler ones found in petroleum. One would go far beyond such applications as mingling mercaptans with illuminating gas (about ten pounds per million cubic feet) to detect leaks and the like (208). It is rather surprising that of scores of patents for "sweetening" oils, almost all deal with the conversion of mercaptans to disulfides and not their removal (210, 209, 118, 54). Caustic washing removes completely only methyl and ethyl mercaptans. As for the rest they travel on to be consumed in gasoline or to be treated out by wasteful chemical means.

We should like to close our review with the prediction that we are only at the threshold of a renaissance of interest in mercaptan chemistry.

## VI. CONDENSED LIST OF SUGGESTED RESEARCH PROBLEMS

1. A critical examination and determination of fundamental physical constants of representative mercaptans.
2. Studies on physical state, association, light absorption and scattering, etc.
3. Thermodynamic data on a selected series.
4. Physical studies on conductivity, dielectric behavior and ionization.
5. Study of hydrate and addition compound formation.
6. Adsorption on surfaces.
7. Distribution between solvents.
8. A detailed investigation of thermal decomposition.
9. Decomposition by physical agencies other than thermal.
10. Comparative study of principal reactions, such as esterification, of alcohols, phenols and mercaptans from a physicochemical point of view.
11. Quantitative investigation of mercaptan-disulfide equilibria in oxidation-reduction systems.

12. The autoxidation of mercaptans and peroxide formation.

13. An investigation of the mechanism of decomposition reactions which lead directly to the formation of mercaptans.

14. Study on orientation of substituting groups in aromatic mercaptan types and the like to determine relative influences.

15. Development of analytical methods with a view toward extending them and rendering them more useful in research.

16. Development of methods for the complete extraction and fractionation of mercaptans from commercial sources.

17. Utilization of commercially extracted mercaptan mixtures.

Acknowledgment: We should like to express our appreciation of the criticism and encouragement received by us from Drs. J. B. Hill and L. M. Henderson.

REFERENCES

(1) OBERMEYER: Ber. **20**, 2918 (1887).
(2) BINZ, RÖTH AND WALTER: Ber. **57**, 1398 (1924).
(3) GABRIEL AND COLMAN: Ber. **45**, 1643 (1912).
(4) TABOURY: Bull. soc. chim. [3] **29**, 761 (1903).
(5) TABOURY: Chem. Zentr. **1908**, II, 1349.
(6) DELEPINE: Bull. soc. chim. [3] **29**, 48 (1903).
(7) KRAFFT AND SCHÖNHERR: Ber. **22**, 821 (1889).
(7a) STENHOUSE: Ann. **149**, 247 (1869).
(8) ZINCKE AND JÖRG: Ber. **42**, 3362 (1909).
(8a) HINSBERG: Ber. **39**, 2431 (1906).
(8b) GIBSON AND SMILES: J. Chem. Soc. **121**, 2388 (1923).
(8c) BAUMANN AND FROMM: Ber. **24**, 1441 (1891).
(9) KELBER AND SCHWARZ: Ber. **44**, 1693 (1911).
(10) ARNDT AND ROSENAU: Ber. **50**, 1248 (1917).
(11) EDINGER: Ber. **41**, 937 (1908).
(12) APITZSCH AND KELBER: Ber. **43**, 1259 (1910).
(13) GATTERMANN: Ann. **393**, 113 (1912).
(13a) LAMBRECHT AND WEIL: Ber. **38**, 270 (1905).
(14) BRAUN: Ber. **42**, 4568 (1909).
(15) ZINCKE AND FROHNEBERG: Ber. **42**, 2721 (1909).
(16) HEFFTER: Ber. **28**, 2258 (1895).
(16a) PIEVERLING: Ann. **183**, 344 (1876).
(16b) ROOS: Ber. **21**, 619 (1888).
(16c) KÖTZ: Ber. **33**, 729 (1900).
(17) MARCKWALD, KLEMM AND TRABERT: Ber. **33**, 1556 (1900).
(18) WREDE: Z. physiol. Chem. **119**, 46 (1922).
(19) HAGELBERG: Ber. **23**, 1083 (1890).

(19a) BENNETT: J. Chem. Soc. **119,** 423 (1921); **121,** 2139 (1923).
(19b) FRIEDEL AND LADENBURG: Ann. **145,** 179 (1868).
(20) TIMMERMANS AND MATTAAR: Chem. Zentr. **1921,** III, 1266.
(21) DELEPINE: Ann. chim. phys. [8] **25,** 529 (1912).
(21a) ARNDT, MILDE AND ECKERT: Ber. **54B,** 2236 (1921).
(22) NASINI: Ber. **15,** 2878 (1882).
(22a) BORGSTROM AND MCINTIRE: Ind. Eng. Chem. **22,** 253 (1930).
(22b) CARRARA AND COPPADORO: Gazz. chim. ital. **33** I, 329 (1903).
(22c) VESPIGNANI: Gazz. chim. ital. **33** I, 73 (1903).
(22d) FERRETTO: Gazz. chim. ital. **30** I, 296 (1900).
(23) KLASON: Ber. **20,** 3407 (1887).
(24) BRAUN AND ENGELBERTZ: Ber. **56,** 1573 (1923).
(24a) KIMBALL AND REID: J. Am. Chem. Soc. **38,** 2757 (1916).
(24b) BENNETT AND STORY: Oil Gas J. **25,** No. 48, 162 (1927).
(25) ADAMS, BRAMLET AND JENDICK: J. Am. Chem. Soc. **42,** 2369 (1920).
(26) HENRY: Chem. Zentr. **1905,** II, 214.
(27) MEYER, VICTOR: Ber. **19,** 3259 (1886).
(28) BRAUN: Ber. **45,** 1563 (1912).
(29) CAHOURS AND HOFFMANN: Ann. **102,** 292 (1857).
(29a) GERLICH: Ann. **178,** 88 (1875).
(30) WUYTS: Bull. soc. chim. [3] **35,** 166 (1906).
(30a) WUYTS AND COSYNS: Bull. soc. chim. [3] **29,** 689 (1903).
(30b) EISENLOHR: Ber. **44,** 3188 (1911).
(31) OTTO AND RÖSSING: Ber. **19,** 3129 (1886).
(32) VOGT: Ann. **119,** 142 (1861).
(32a) MÄRKER: Ann. **136,** 75 (1865).
(33) AUTENRIETH AND BEUTTEL: Ber. **42,** 4357 (1909).
(34) ZINCKE AND EISMAYER: Ber. **51,** 751 (1918).
(35) GILMAN AND DICKEY: J. Am. Chem. Soc. **52,** 2141 (1930).
(36) CHELINZER: Bull. soc. chim. [4] **37,** 176 (1925).
(37) RECHENBERG: J. prakt. Chem. **101,** 112 (1920).
(38) BERTHOUD AND BRUM: J. chim. phys. **21,** 143 (1924).
(39) YOUNG, SIDNEY: Distillation Principles and Processes, p. 53. Macmillan and Company, New York (1922).
(40) PRICE AND TWISS: J. Chem. Soc. **101,** 1259 (1912).
(40a) BRJUCHONENKO: J. prakt. Chem. [2] **59,** 46 (1899).
(40b) HENRY AND DEWAEL: Chem. Zentr. **1909,** I, 1854.
(40c) PEXSTERS: Chem. Zentr. **1907,** I, 1398.
(41) VOTOCEK AND VESELY: Ber. **47,** 1515 (1914).
(42) SCHNEIDER, GILLE AND EISFELD: Ber. **61B,** 1244 (1928).
(43) FOX AND POPE: J. Chem. Soc. **103,** 1263 (1913).
(44) HANTZSCH AND BUCERIUS: Ber. **59B,** 793 (1926).
(44a) KLASON AND CARLSON: Ber. **39,** 738 (1906).
(45) HILDEBRAND: Solubility. The Chemical Catalog Company, New York (1924).
(46) DUNSTAN: Z. physik. Chem. **49,** 590 (1904).
(47) HARKINS, CLARK, AND ROBERTS: J. Am. Chem. Soc. **42,** 700 (1920).
(47a) HARKINS AND OTHERS: J. Am. Chem. Soc. **39,** 356, 363, 560, 575, 581 (1917).

(48) WALDEN: Z. physik. Chem. **66,** 385 (1909).
(48a) BINGHAM AND FORNWALT: Science **71,** 564 (1930).
(49) BRUNI AND TROVANELLI: Gazz. chim. ital. **34** II, 349 (1904).
(50) CLAESSON: J. prakt. Chem. [2] **15,** 193 (1877).
(51) CARIUS: Ann. **124,** 260 (1862).
(51a) ROSEN AND REIL: J. Am. Chem. Soc. **44,** 634 (1922).
(52) WILLGERODT: Ber. **18,** 331 (1885).
(53) VORLÄNDER AND MITTAG: Ber. **46,** 3450 (1913).
(54) GREER: Ind. Eng. Chem. **21,** 1033 (1929).
(55) BORGSTROM AND OTHERS: Ind. Eng. Chem. **22,** 245 (1930).
(56) ERLENMEYER AND WANKLYN: Ann. **135,** 129 (1865).
(57) KINDLER AND FINNDORF: Ber. **54,** 1079 (1921).
(57a) FISCHER: Ann. **190,** 118 (1877).
(57b) KELBER AND SCHWARZ: Ber. **45,** 137 (1912).
(57c) FARAGHER, MORRELL AND COMAY: Ind. Eng. Chem. **20,** 527 (1928).
(57d) WILLGERODT: Ber. **17,** Ref., 353 (1884).
(57e) BROWNE AND HOEL: J. Am. Chem. Soc. **44,** 2315 (1922).
(57f) HINSBERG: Ber. **43,** 1874 (1910).
(57g) KLASON: J. prakt. Chem. [2] **33,** 115 (1886).
(57h) CHAPMAN: J. Chem. Soc. **1928,** 1894.
(57i) KOELSCH: J. Am. Chem. Soc. **52,** 1105 (1930).
(57j) ZINCKE AND SCHÜTZ: Ber. **45,** 475 (1912).
(57k) HESS: Ber. **14,** 488 (1884).
(57l) BOST AND MATTOX: J. Am. Chem. Soc. **52,** 332 (1930).
(57m) HINSBERG: Ber. **43,** 651 (1910).
(57n) WATERMANN AND VAN TUSSENBROEK: Erdöl Teer **3,** 743 (1927).
(58) SABATIER AND MAILHE: Compt. rend. **150,** 1569 (1910).
(58a) SABATIER (REID): Catalysis in Organic Chemistry, p. 622. D. Van Nostrand Company, New York (1923).
(59) OTTO: Ber. **13,** 1289 (1880).
(59a) LECHER AND LIEFKEN: Ber. **59,** 1314 (1926).
(59b) OTTO, LÖWENTHAL AND GRUBER: Ann. **149,** 101 (1869).
(59c) DREHER AND OTTO: Ann. **154,** 178 (1870).
(59d) DREHER AND OTTO: Ann. **154,** 93 (1870).
(59e) WOOD: J. Am. Chem. Soc. **47,** 2062 (1925).
(59f) STENHOUSE: Ann. **140,** 284 (1866); **149,** 247 (1869).
(59g) LECHER: Ber. **48,** 1425 (1915).
(59h) RABAAT: Bull. soc. chim. [3] **27,** 690 (1902).
(59i) GABRIEL AND DEUTSCH: Ber. **13,** 386 (1883).
(59j) WOOD, LOWY AND FARAGHER: Ind. Eng. Chem. **16,** 1116 (1924).
(60) BORGSTROM, ROSEMAN AND REID: Ind. Eng. Chem. **22,** 248 (1930).
(61) HURD: Pyrolysis of Carbon Compounds, p. 699. Chemical Catalog Company, New York (1929).
(62) FICHTER AND BRAUN: Ber. **47,** 1526 (1914).
(62a) FICHTER AND WENK: Ber. **45,** 1373 (1912).
(63) GOLDSCHMIDT AND WEISSLER: Ber. **23,** 272 (1890).
(64) RAY: J. Chem. Soc. **115,** 871 (1919).
(64a) DAINS, ROBERTS AND BREWSTER: J. Am. Chem. Soc. **38,** 131 (1916).

(65) RAY AND DEY: J. Chem. Soc. **109,** 698 (1916).
(66) HANTZSCH AND WOLVEKAMP: Ann. **331,** 265 (1904).
(67) LESSER AND GAD: Ber. **56B,** 963 (1923).
(68) LEVENE AND MIKESKA: J. Biol. Chem. **59,** 473 (1924).
(68a) LEVENE AND MIKESKA: J. Biol. Chem. **63,** 85 (1925).
(68b) LEVENE AND MIKESKA: J. Biol. Chem. **70,** 365 (1926).
(68c) LEVENE AND MORI: J. Biol. Chem. **78,** 1 (1928).
(69) Files of the authors.
(70) POSNER: Ber. **38,** 646 (1905).
(70a) POSNER: Ber. **37,** 502 (1904).
(71) RUHEMANN: J. Chem. Soc. **87,** 461 (1905).
(72) GABRIEL AND HEYMANN: Ber. **24,** 783 (1891).
(73) MARCKWALD: Ber. **25,** 2354 (1892).
(74) BAUMANN: Ber. **18,** 883 (1885).
(74a) BAUMANN: Ber. **18,** 258 (1885).
(74b) BENNETT AND WHINCOP: J. Chem. Soc. **119,** 422 (1921).
(75) GATTERMAN: Ber. **31,** 1765 (1898); **32,** 271 (1899).
(75a) GATTERMAN: Ann. **357,** 363 (1907).
(76) STEINKOPF AND MÜLLER: Ber. **56,** 1930 (1923).
(76a) PINNER AND KLEIN: Ber. **11,** 1825 (1878).
(76b) SCHMIDT: Ber. **47,** 2545 (1914).
(76c) BERNTHSEN: Ann. **197,** 341 (1879).
(76d) LUCKENBACH: Ber. **17,** 1428 (1884).
(77) SCHONBERG, SCHÜTZ, ARNDT AND PETER: Ber. **60B,** 2344 (1927).
(77a) POSNER: Ann. **336,** 86 (1904).
(78) ESCALES AND BAUMANN: Ber. **19,** 1787 (1886).
(78a) RUHEMANN: J. Chem. Soc. **87,** 17 (1905).
(78b) FASBENDER: Ber. **20,** 460 (1887).
(78c) POSNER: Ber. **40,** 4788 (1907).
(78d) BONGARTZ: Ber. **19,** 1931 (1886); **21,** 478 (1888).
(79) FROMM AND JÖRG: Ber. **58B,** 304 (1925).
(80) DIELS AND WULFF: Ann. **437,** 309 (1924).
(81) FROMM AND ERFURT: Ber. **42,** 3808 (1909).
(81a) WERNER: J. Chem. Soc. **101,** 2166 (1912).
(81b) AUWERS AND ARNDT: Ber. **42,** 2713 (1909).
(82) PAULY, SCHÜBEL AND LOCKEMANN: Ann. **383,** 288 (1911).
(82a) AUTENRIETH AND HENNINGS: Ber. **35,** 1388 (1902).
(82b) CLAASZ: Ber. **45,** 1015 (1912).
(82c) WHITNER AND REID: J. Am. Chem. Soc. **43,** 636 (1921).
(82d) PAULY AND BUTTLAR: Ann. **383,** 272 (1911).
(82e) SCHNEIDER: Ann. **386,** 348 (1911).
(82f) KELBER: Ber. **45,** 2484 (1912).
(82g) STUFFER: Ber. **23,** 1408, 3226 (1890).
(82h) FROMM AND JÖRG: Ber. **58B,** 304 (1925).
(82i) BAUMANN AND WATTER: Ber. **26,** 1124 (1893).
(82j) FROMM AND WITMANN: Ber. **41,** 2264 (1908).
(82k) FROMM, FÖRSTER AND SCHERSCHEWIZKI: Ann. **394,** 243 (1912).
(82l) HOUBEN AND SCHULTZE: Ber. **44,** 3235 (1911).

(82m) McLeod and Robinson: J. Chem. Soc. **119,** 1470 (1921).
(83) Autenrieth: Ber. **24,** 166 (1891).
(83a) Posner: Ber. **33,** 2983 (1900).
(83b) Swallen and Boord: J. Am. Chem. Soc. **52,** 651 (1930).
(83c) Posner: Ber. **34,** 1395 (1901).
(83d) Posner: Ber. **37,** 502 (1904).
(83e) Recsei: Ber. **60,** 1420 (1927).
(83f) Bayer and Co.: Ber. **22** Ref., 115 (1889); German pat. 46,333.
(83g) Recsei: Ber. **60B,** 1836 (1927).
(84) Fischer: Ber. **27,** 673 (1894).
(84a) Fischer and Delbrück: Ber. **42,** 1476 (1909).
(84b) Schneider, Sepp and Stiehler: Ber. **51,** 220 (1918).
(84c) Fischer, Helferich and Ostmann: Ber. **53,** 873 (1920).
(84d) Purves: J. Am. Chem. Soc. **51,** 3619 (1929).
(85) Holmberg: Ber. **45,** 364 (1912).
(85a) Holmberg: Ber. **40,** 1740 (1907).
(85b) Houben: Ber. **45,** 2942 (1912).
(85c) Zincke and Brune: Ber. **44,** 185 (1911).
(85d) Pollak and Schädler: J. Chem. Soc. **114,** 497 (1918).
(85e) Pollak, Fiedler and Roth: J. Chem. Soc. **114,** 498 (1918).
(85f) Faber and Reid: J. Am. Chem. Soc. **39,** 1930 (1917).
(85g) Pratt and Reid: J. Am. Chem. Soc. **37,** 1934 (1915).
(85h) Sachs and Reid: J. Am. Chem. Soc. **38,** 2746 (1916).
(86) Mylius: Ber. **49,** 1091 (1916).
(87) Reid: Am. Chem. J. **43,** 489 (1910).
(88) Gabriel: Ber. **10,** 1857 (1877).
(88a) Krishna and Singh: Quart. J. Indian Chem. Soc. **4,** 291 (1927).
(89) Ray: J. Chem. Soc. **109,** 131 (1916).
(90) Manchot and Gall: Ber. **60,** 2318 (1927).
(91) Autenrieth: Ann. **259,** 362 (1890).
(92) Salomon: J. prakt. Chem. [2] **7,** 252 (1873).
(92a) Klason: Ber. **20,** 2384 (1887).
(92b) Klason: Ber. **20,** 3407 (1887).
(93) Salomon: J. prakt. Chem. [2] **6,** 433 (1873).
(94) Schwarze: J. prakt. Chem. [2] **10,** 222 (1874).
(96) Jones and Tasker: J. Chem. Soc. **95,** 1904 (1909).
(97) Gibson and Smiles: J. Chem. Soc. **123,** 2388 (1923).
(97a) Mauthner: Ber. **38,** 1411 (1905).
(97b) Autenrieth and Geyer: Ber. **41,** 4249 (1908).
(97c) Kelber: Ber. **43,** 1252 (1910).
(97d) Ullmann: Ber. **43,** 536 (1910).
(97e) Zincke and Kempf: Ber. **44,** 413 (1911).
(97f) Lecher: Ber. **53,** 591 (1920).
(97g) Böse: Ber. **53B,** 2000 (1920).
(97h) Helfrich and Reid: J. Am. Chem. Soc. **42,** 1208 (1920).
(97i) Lecher: Ber. **48,** 524 (1915).
(97j) Wahl: Ber. **55B,** 1449 (1922).
(97k) Fromm and Ungar: Ber. **56,** 2287 (1923).

(97l) Otto and Lüders: Ber. **13**, 1283 (1880).
(97m) Lecher and Holschneider: Ber. **57**, 755 (1924).
(97n) Bennett and Berry: J. Chem. Soc. **1927**, 1666.
(97o) Claesson: Bull. soc. chim. [2] **25**, 183 (1876).
(97p) Ray: J. Chem. Soc. **123**, 133 (1923).
(98) Saizens: Ann. **139**, 354 (1866); **144**, 148 (1867).
(98a) Krüger: J. prakt. Chem. [2] **14**, 193 (1876).
(98b) Lecher and Wittwer: Ber. **55B**, 1474 (1922).
(98c) Fromm, Benzinger and Schäfer: Ann. **394**, 325 (1912).
(98d) Sachs, Schlesinger and Antoine: Ann. **433**, 154 (1923).
(98e) Pollak and Carniol: Ber. **42**, 3252 (1909).
(98f) Pummerer: Ber. **43**, 1401 (1910).
(98g) Bourgeois and Huber: Bull. soc. chim. [4] **9**, 944 (1912).
(98h) Zincke and Krüger: Ber. **45**, 3468 (1912).
(98i) Brand and Wirsing: Ber. **45**, 1757 (1912).
(98j) Brand and Wirsing: Ber. **46**, 820 (1913).
(98k) Steinkopf, Herold and Stohr: Ber. **53**, 1007 (1920).
(98l) Loevenich, Utseh, Moldrickx and Schaeffer: Ber. **62**, 3084 (1929).
(98m) Braun and Engelbertz: Ber. **56B**, 1573 (1923).
(98n) Otto: Ber. **13**, 1272 (1880).
(98o) Vorländer and Mittag: Ber. **52**, 413 (1919).
(98p) Carlson: Chem. Zentr. **1908**, I, 934; Arkiv. Kemi Mineral. Geol. **3**, No. 8, 1 (1908).
(98q) Autenrieth and Beuttel: Ber. **42**, 4346 (1909).
(98r) Kehrmann and Sava: Ber. **45**, 2895 (1912).
(98s) Zincke and Dahm: Ber. **45**, 3457 (1912).
(98t) Lecher and Simon: Ber. **54**, 632 (1921).
(98u) Rosen and Reid: J. Am. Chem. Soc. **44**, 634 (1922).
(98v) Gilman and Beaber: J. Am. Chem. Soc. **47**, 1449 (1925).
(98w) Shriner, Struck and Jorison: J. Am. Chem. Soc. **52**, 2060 (1930).
(98x) Steinkopf, Herold and Stöhr: Ber. **53**, 1007 (1920).
(99) Städler: Ber. **17**, 2075 (1884).
(99a) Ziegler: Ber. **23**, 2470 (1890).
(99b) Mayer: Ber. **42**, 3046 (1909).
(100) Hixson and Cauwenberg: J. Am. Chem. Soc. **52**, 2125 (1930).
(100a) Scheibler and Voss: Ber. **53**, 379 (1920).
(100b) Claasz: Ber. **45**, 747 (1912).
(100c) Krollpfeiffer and Schultze: Ber. **56**, 1819 (1923).
(100d) Michael and Schulthess: J. prakt. Chem. [2] **46**, 236 (1892).
(100e) Reid, Mackall and Miller: J. Am. Chem. Soc. **43**, 2104 (1921).
(100f) Schaarschmidt: Ann. **409**, 59 (1915).
(100g) Hoffman and Reid: J. Am. Chem. Soc. **45**, 1831 (1923).
(101) Jacobson, Kwaysser, Janssen, Ney and Schwartz: Ann. **277**, 209 (1893).
(101a) Gabriel and Heymann: Ber. **23**, 157 (1890).
(101b) Gabriel: Ber. **22**, 1110 (1891).
(101c) Hilditch: J. Chem. Soc. **97**, 2579 (1910).
(101d) Braun: Ber. **43**, 3220 (1910).
(101e) Ray: J. Chem. Soc. **125**, 1141 (1925).

(102a) BENNETT: J. Chem. Soc. **121,** 2139 (1922).
(102b) SCHILLER AND OTTO: Ber. **9,** 1588, 1638 (1876).
(102c) LAGAI: Ber. **25,** 1836 (1892).
(102d) PRESCOTT AND SMILES: J. Chem. Soc. **99,** 640 (1911).
(102e) ERLENMEYER AND LISENKO: Jahresber. Pharm. **1861,** 590.
(103) FRIES AND VOLK: Ber. **42,** 1170 (1909).
(104) BIRCH AND NORRIS: Ind. Eng. Chem. **21,** 1087 (1929).
(105) LÖWIG, WEIDMANN AND KOPP: Ann. **35,** 343 (1840).
(105a) LÖWIG AND WEIDMANN: Pogg. Ann. **49,** 323 (1840).
(105b) GRABOWSKY: Ann. **175,** 344 (1875).
(105c) GRABOWSKY AND SAYTZEFF: Ann. **171,** 251 (1874).
(105d) MYLIUS: Ber. **5,** 978 (1872).
(105e) BESTHORN AND GEISSELBRECHT: Ber. **53,** 1017 (1920).
(105f) BEILSTEIN AND KURBATOW: Ann. **197,** 75 (1879).
(106) ANSCHÜTZ: Ann. **284,** 9 (1895).
(107) FISCHER AND BRIEGER: Ber. **47,** 2477 (1914).
(108) RHEINBOLDT: Ber. **59B,** 1311 (1926).
(109) REYCHLER: Bull. soc. chim. Belg. **27,** 110 (1913).
(109a) NORRIS, FALKNER AND PRICE: J. Chem. Soc. **121,** 2161 (1922).
(110) TRAUBE: Ann. **331,** 64 (1904).
(110a) BARNETT: J. Chem. Soc. **97,** 63 (1910).
(110b) FRIES AND KERKOW: Ann. **427,** 281 (1922).
(111) LOVÉN: J. prakt. Chem. [2] **29,** 366 (1884).
(112) MICHAELIS AND LINKE: Ber. **40,** 3419 (1907).
(113) ROHRBACH: Ann. **315,** 13 (1901).
(114) ERLENMEYER: Ber. **36,** 2720 (1903).
(114a) FICHTER AND BECK: Ber. **44,** 3636 (1911).
(114b) ZINCKE: Ann. **400,** 8 (1914).
(114c) CHILD AND SMILES: J. Chem. Soc. **1926,** 2696.
(115) SCHERTEL: Ann. **132,** 91 (1864).
(115a) STENHOUSE: Ann. **149,** 247 (1869).
(115b) OTTO AND RÖSSING: Ber. **18,** 2493 (1885); **19,** 3129 (1886).
(115c) FICHTER AND BERNOULLI: Ber. **42,** 4308 (1909).
(115d) RAY: J. Chem. Soc. **117,** 1090 (1920).
(116) SCHWARZ AND MÜNCHMEYER: Chem. Zentr. **1914,** I, 56.
(117) TABOURY: Ann. chim. [8] **15,** 48 (1908).
(118) WENDT AND DIGGS: Ind. Eng. Chem. **16,** 1113 (1924).
(118a) HOLMBERG: Ann. **359,** 81 (1907).
(118b) OTT AND REID: Ind. Eng. Chem. **22,** 878 (1930).
(118c) BÖTTGER: Ann. **223,** 346 (1884).
(118d) MÜLLER: J. prakt. Chem. [2] **4,** 39 (1871).
(118e) GLASS AND REID: J. Am. Chem. Soc. **51,** 3428 (1929).
(118f) HAITINGER: Monatsh. **4,** 165 (1883).
(119) HÜBNER AND ALSBERG: Ann. **156,** 330 (1870).
(119a) CLAESSON: Ber. **14,** 409 (1881).
(119b) KEKULÉ AND LINNEMANN: Ann. **123,** 277 (1862).
(119c) OTTO AND TRÖGER: Ber. **24,** 1145 (1891).
(119d) COBLENTZ AND GABRIEL: Ber. **24,** 1122 (1891).

(119e) BIILMANN: Ann. **339**, 351 (1905).
(119f) BIILMANN: Ann. **348**, 120 (1906).
(120) FASBENDER: Ber. **21**, 1470 (1888).
(120a) GABRIEL AND LAUER: Ber. **23**, 82 (1890).
(120b) TEBOURY: Bull. soc. chim. [4] **1**, 741 (1907).
(120c) LECHER AND SIMON: Ber. **58**, 409 (1925).
(121) BIRCH AND NORRIS: J. Chem. Soc. **127**, 1934 (1925).
(121a) POLLAK AND RIESZ: Monatsh. **53**, and **54**, 90 (1929).
(122) COURANT AND RICHTER: Ber. **18**, 3178 (1885).
(123) RICHTER: Ber. **49**, 1026 (1916).
(123a) SMYTHE AND FORSTER: J. Chem. Soc. **97**, 1195 (1910).
(124) TROEGER AND HORNUNG: J. prakt. Chem. [2] **60**, 113 (1899).
(124a) CLAESSON: Bull. soc. chim. [2] **25**, 183 (1876).
(124b) LEVI AND BARONI: Atti accad. Lincei [6] **9**, 772 (1929).
(124c) CHAKRAVARTI: J. Chem. Soc. **123**, 964 (1923).
(124d) LECHER: Ber. **58**, 417 (1925).
(124e) OTTO: J. prakt. Chem. [2] **37**, 207 (1888).
(125) NEKRASOV AND MELNIKOV: Ber. **62B**, 2091 (1929).
(125a) FRIES, HASSELBROCK AND SCHRÖDER: Ber. **47**, 1640 (1914).
(126) BINZ AND HOLZAPFEL: Ber. **53**, 2017 (1920).
(127) BECKURTS AND OTTO: Ber. **11**, 2061 (1878).
(128) TARBOURIECH: Bull. soc. chim. [3] **25**, 313 (1901).
(128a) BONGARTZ: Ber. **21**, 478 (1888).
(128b) WICHELHAUS, Ber. **5**, 850 (1872).
(129) SMYTHE: Proc. Univ. Durham Phil. Soc. **4**, Part 4, 220 (1912).
(130) HOLMBERG: Ber. **43**, 226 (1910).
(131) ENGLER AND BRONIATOWSKI: Ber. **37**, 3274 (1904).
(132) APITZSCH AND BAUER: Ber. **41**, 4039 (1908).
(132a) ALBRECHT: Ann. **161**, 129 (1872).
(132b) FITTICA: Ann. **172**, 303 (1874).
(132c) OTTO AND RÖSSING: Ber. **25**, 988 (1892).
(132d) WISSINGER: Ber. **20**, Ref., 364 (1887).
(132e) PRICE AND TWISS: J. Chem. Soc. **95**, 1725 (1909).
(132f) COBLENTZ AND GABRIEL: Ber. **22**, 1122 (1889).
(132g) ZINCKE AND JÖRG: Ber. **43**, 3443 (1910).
(132h) BRAUN AND TRÜMPLER: Ber. **43**, 545 (1910).
(132i) BRAND AND WIRSING: Ber **46**, 820 (1913).
(132j) FREUDENBERG AND WOLF: Ber. **60**, 232 (1927).
(133) WUYTS: Bull. soc. chim. [4] **5**, 405 (1909).
(133a) HEPWORTH AND CLAPHAM: J. Chem. Soc. **119**, 1188 (1921).
(134) GABRIEL: Ber. **22**, 1137 (1889).
(135) KINDLER AND DEHN: Ber. **54**, 1080 (1921).
(136) GUTMANN: Ber. **48**, 1162 (1915).
(137) NAKAMURA: Biochem. Z. **164**, 31 (1925).
(137a) NENCKI AND LIEBER: Monatsh. **10**, 526 (1889).
(137b) SALKOWSKI: Biochem. Z. **79**, 68 (1917).
(137c) GAUTIER: Compt. rend. soc. biol. **89**, 239 (1923).
(137d) NENCKI: Monatsh. **10**, 862 (1889).

(137e) SUTER: Z. physiol. Chem. **20,** 564 (1895).
(137f) PORCHER AND HERVIEUX: Compt. rend soc. biol. **68,** 27 (1910).
(137g) MÖRNER: Z. physiol. Chem. **42,** 365 (1904).
(138) NEUBERG AND NORD: Ber. **47,** 2264 (1914).
(138a) KONDO: Biochem. Z. **136,** 198 (1923).
(138b) NEUBERG AND NORD: Biochem. Z. **67,** 46 (1914).
(138c) NEUBERG AND SCHWENK: Biochem. Z. **71,** 118 (1915).
(138d) NORD: Ber. **52B,** 1207 (1919).
(138e) MATHIEU: Ann. brasserie distillerie **1911,** 329.
(138f) MATHIEU: Bull. l'assoc. chim. sucr. dist. **28,** 971 (1912).
(139) LEWIS AND MCGINTY: J. Biol. Chem. **53,** 349 (1922).
(139a) LEWIS, UPDEGRAFF AND MCGINTY: J. Biol. Chem. **59,** 59 (1924).
(139b) BIERICH AND KALBE: Z. physiol. Chem. **158,** 1 (1926).
(139c) GATEWOOD AND JOHNSON: J. Am. Chem. Soc. **48,** 2900 (1926).
(139d) HILL AND LEWIS: J. Biol. Chem. **59,** 557, 569 (1924)
(139e) OKUDA AND KATU: J. Agr. Chem. Soc. Japan **5,** 549 (1929).
(140) BROWN AND SNYDER: J. Am. Chem. Soc. **48,** 1926 (1926).
(141) KIERZEK: Bull. soc. chim. [4] **41,** 1299 (1927).
(141a) ZEISE: Ann. **11,** 1 (1834).
(141b) RAY, CHAKRAVARTI AND BOSE: J. Chem. Soc. **123,** 1957 (1923).
(141c) SCHNEIDER AND WREDE: Ber. **50,** 793 (1917).
(141d) DUVILLIER: Bull. soc. chim [2] **30,** 506 (1878).
(141e) AUTENRIETH AND GEYER: Ber. **41,** 4249 (1908).
(141f) BIILMAN: Ann. **339,** 351 (1905).
(141g) BLOCH AND BERGMANN: Ber. **53B,** 961 (1920).
(141h) KOENIGS AND KINNE: Ber. **54,** 1357 (1921).
(141i) GREGORY: Ann. **15,** 239 (1835).
(141j) AUDREASCH: Ber. **12,** 1390 (1879).
(141k) PURGOTTI: Gazz. chim. ital. **20,** 24 (1890).
(141l) GUTMANN: Ber. **54,** 1410 (1921).
(141m) FLESCH: Ber. **6,** 428 (1873).
(141n) FENAU: Quim. ind. **2,** 169 (1925).
(141o) REISSERT AND HOLLE: Ber. **44,** 3027 (1911).
(141p) LEVI: Atti accad. Lincei [6] **9,** 170 (1929).
(141q) HÖHN AND BLOCK: J. prakt. Chem. [2] **82,** 486 (1910).
(141r) SCHNEIDER AND BEUTHER: Ber. **52B,** 2135 (1919).
(141s) SCHNEIDER: Ber. **49,** 1638 (1916).
(141t) SCHNEIDER AND STREBLER: Ber. **52,** 2131 (1919).
(142) BING AND RÖTH: Ber. **58B,** 309 (1925).
(143) MEREZHKOVSKY: J. Russ. Phys. Chem. Soc. **46,** 1082 (1914).
(144) MAUTHNER: Ber. **39,** 1347 (1906).
(144a) LEUCKHARDT: German pat. 45,120. Mar. 25, 1887. Ber. **21,** Ref., 915 (1888).
(144b) LEUCKHARDT: J. prakt. Chem. [2] **41,** 179 (1890).
(144c) FRIEDLÄNDER AND MAUTHNER: Chem. Zentr. **1904,** II, 1176.
(145) CHICHIBABIN AND BAGDASSARJANZ: J. prakt. Chem. **108,** 200 (1924).
(146) MAILHE: Bull. soc. chim. [4] **15,** 327 (1915).
(146a) KRAMER AND REID: J. Am. Chem. Soc. **43,** 880 (1921).
(146b) GILFILLAN: J. Am. Chem. Soc. **44,** 1323 (1922).

(147) FROMM, HAAS AND HUBERT: Ann. **394**, 290 (1912).
(148) KEKULÉ: Z. für Chem. **1867**, 193; Ann. **90**, 309 (1854).
(148a) ENGLER: Ber. **11**, 926 (1878).
(148b) KOWALEWSKY: Ann. **119**, 303 (1861).
(148c) PISHCHIMUKA: J. Chim. Ukraine: Jour. Russ. Phys. Chem. Soc. **56**, 11 (1925); C. A. **19**, 2808; **20**, 2816.
(149) DEBUS: Ann. **72**, 1 (1849).
(149a) DEBUS: Ann. **75**, 121 (1850).
(149b) TSCHUGAEFF AND GASTEFF: Ber. **42**, 4631 (1909).
(150) BAUMANN AND PREUSSE: Z. physiol. Chem. **5**, 309 (1881).
(151) APITZSCH: Ber. **37**, 1599 (1904).
(151a) APITZSCH: Ber. **41**, 4028 (1908).
(151b) GABRIEL AND OHLE: Ber. **50**, 804 (1917).
(151c) BUSCH ET AL: J. prakt. Chem. [2] **93**, 25 (1916).
(151d) BEDFORD AND SABRELL: Ind. Eng. Chem. **13**, 1034 (1921).
(151e) SEBRELL AND BOORD: J. Am. Chem. Soc. **45**, 2390 (1923).
(152) LIEBERMANN AND LANGE: Ber. **12**, 1588 (1879).
(153) BRAND, STELLMANN, GROEBE AND STEIN: J. prakt. Chem. [2] **109**, 1 (1925).
(154) TAYLOR: J. Chem. Soc. **111**, 655 (1917).
(154a) RATHKE: Ber. **17**, 297 (1884).
(155) PLUMMERER: Ber. **42**, 2282 (1909).
(156) POGGI: Atti accad. Lincei [6] **2**, 423 (1925).
(157) TABOURY: Bull. soc. chim. [3] **29**, 761 (1903).
(157a) TABOURY: Bull. soc. chim. [3] **33**, 836 (1905).
(157b) BORSCHE AND LANGER: Ber. **39**, 2346 (1906).
(158) SCHNEIDER, CLIBBENS, HÜLLWECK AND STEIBELT: Ber. **47**, 1258 (1914).
(159) SCHMITT AND GLUTZ: Ber. **1**, 166 (1868).
(159a) HOFMANN: Ber. **1**, 169 (1868).
(160) WEISSGERBER AND SEIDLER: Ber. **60B**, 2088 (1927).
(161) REISSERT AND MANUS: Ber. **61B**, 1308 (1928).
(161a) FROMM AND FÖRSTER: Ann. **394**, 338 (1912).
(161b) OTTO AND RÖSSING: Ber. **19**, 3132 (1886).
(161c) OTTO AND RÖSSING: Ber. **19**, 1235 (1886).
(161d) FROMM AND ROESICKE: Ber. **41**, 3397 (1908).
(162) SCHÖNE: J. prakt. Chem. [2] **30**, 416 (1885).
(162a) SCHÖNE: J. prakt. Chem. [2] **32**, 241 (1885).
(162b) OTTO AND HEYDECKE: Ber. **25**, 1477 (1892).
(162c) WORRALL: J. Am. Chem. Soc. **40**, 415 (1918).
(162d) PLOTNIKOV: J. Russ. Phys. Chem. Soc. **45**, 1162 (1913).
(162e) POSNER: Ber. **32**, 2801 (1899).
(162f) HEINTZ: Ann. **136**, 223 (1865).
(162g) HANTZSCH AND FREESE: Ber. **28**, 3237 (1895).
(162h) KNORR: Ber. **50**, 229 (1917).
(163) CLAASZ: Ber. **45**, 2424 (1912).
(163a) I.N.G.A.: Swiss pat. 133,787. Oct. 18, 1927.
(163b) KONEK: Ber. **53B**, 1666 (1920).
(163c) KRAFT AND LYONS: Ber. **27**, 1761 (1894).
(163d) MOSES AND REID: J. Am. Chem. Soc. **48**, 776 (1926).

(163e) GRAY AND GUTEKUNST: J. Am. Chem. Soc. **42**, 856 (1920).
(163f) FROMM AND JÖRG: Ber. **58B**, 304 (1925).
(163g) I. G. FARBENIND. A.-G.: French pat. 642,128 (1927).
(163h) STAUDINGER AND REICHSTEIN: U. S. pat. 1,715,795 (C. A. **23**, 3715).
(163i) COHEN AND SKIRROW: J. Chem. Soc. **75**, 887 (1899).
(164) BRAND: Ber. **42**, 3463 (1909).
(164a) German pat. 228,868 (1910).
(165) GUTMANN: Ber. **47**, 635 (1914).
(166) PAZSCHKE: J. prakt. Chem. [2] **2**, 418 (1870).
(166a) POLLAK: Monatsh. **34**, 1673 (1913).
(166b) HOLTMEYER: Z. für Chem. **1867**, 688.
(166c) RODERBURG: Ber. **6**, 669 (1873).
(166d) POLLAK AND LUCANOVIC: Monatsh. **31**, 695 (1910).
(166e) SPRING: Ber. **7**, 1157 (1874).
(167) LARSSON: Ber. **61B**, 1439 (1928).
(167a) LARSSON: Svensk Kem. Tid. **40**, 149 (1928).
(167b) FICHTER AND TAMM: Ber. **43**, 3032 (1910).
(168) FISCHER, E.: Ber. **48**, 93 (1915).
(168a) CLEVE: Ber. **21**, 1099 (1888).
(169) HILDITCH: Ber. 3583 (1911).
(170) OTTO AND RÖSSING: Ber. **19**, 1224 (1886).
(170a) GATTERMANN: Ber. **32**, 1136 (1899).
(171) FRIES: Ber. **45**, 2965 (1912).
(172) BUNTE: Ber. **7**, 646 (1874).
(173) FRICKE AND FROHNEBERG: Ber. **43**, 837 (1910).
(174) FRICKE AND SPILKER: Ber. **58**, 24, 1589 (1925).
(175) JACOBSON AND NEY: Ann. **277**, 232 (1893).
(176) FRIEDEL AND CRAFTS: Ann. chim. phys. [6] **14**, 433 (1888).
(176a) FRIEDEL AND CRAFTS: Bull. soc. chim. [2] **31**, 463 (1879).
(177) FISCHER: Ber. **10**, 1334 (1877).
(178) BERNTHSEN: Ann. **230**, 73 (1885).
(179) SACHS: Z. anorg. allgem. Chem. **135**, 273 (1924).
(179a) WUYTS: Ber. **36**, 863 (1903).
(180) NENCKI: J. prakt. Chem. [2] **23**, 87 (1881).
(180a) KOTEN AND ADAMS: J. Am. Chem. Soc. **46**, 2764 (1924).
(180b) TCHUGAEV: Ber. **32**, 3333 (1899).
(180c) TCHUGAEV: Ber. **33**, 3120 (1900).
(180d) TCHUGAEV AND FOMIN: Compt. rend. **150**, 1435 (1910).
(180e) BRAUN AND RUMPF: Ber. **35**, 3368 (1902).
(180f) PINNER: Ber. **14**, 1083 (1881).
(181) KLASON AND SEGERFELT: Arkiv Kemi, Mineral. Geol. **4**, No. 6, 20 (1911). Chem. Zentr. **1911**, II, 1616.
(181a) BUSCH AND HOLZMANN: Ber. **34**, 320 (1901).
(181b) AUGER AND BILLY: Compt. rend. **136**, 555 (1903).
(182) SMYTHE: J. Chem. Soc. **121**, 1400 (1921).
(182a) EGLI: Ber. **18**, 575 (1885).
(182b) MEYER, VICTOR: Ber. **16**, 1465 (1883).
(183) LIPPMANN AND FLEISSNER: Monatsh. **9**, 296 (1888).

(184) FROMM, HEYDER, JUNG AND STURM: Ann. **394,** 258 (1912).
(184a) WHEELER AND JAMIESON: J. Biol. Chem. **4,** 111 (1907).
(184b) SCHENCK: Z. physiol. Chem. **77,** 328 (1912).
(185) BAUMANN: Ber. **23,** 1869 (1890).
(186) LENGFELD AND STIEGLITZ: Ber. **28,** 575 (1895).
(187) CLAUS: Ann. **179,** 148 (1875).
(188) RHEINBOLDT: Ber. **60,** 184 (1927).
(189) LECHER AND LIEFKEN: Ber. **59,** 2594 (1926).
(190) ALEXANDER, KILLEN, MACBETH, DAVID, DOIG AND PRATT: J. Chem. Soc. **119,** 354 (1921).
(191) ANDREASCH: Monatsh. **10,** 73 (1889).
(191a) CLAESSON: Ber. **14,** 411 (1881).
(192) SCHACHT: Ann. **129,** 1 (1864).
(192a) BORGSTROM, ELLIS AND REID: J. Am. Chem. Soc. **51,** 3649 (1929).
(192b) RAY AND GUHA: J. Chem. Soc. **115,** 1148 (1919).
(192c) WUYTS AND VANGINDERTAELEN: Bull. soc. chim. Belg. **30,** 323 (1921).
(192d) SACHS: Ber. **53B,** 1737 (1920).
(192e) KLASON: J. prakt. Chem. [2] **67,** 1 (1903).
(192f) SACHS: Ber. **54B,** 1849 (1921).
(192g) RAY: J. Chem. Soc. **121,** 1279 (1922).
(192h) SCHAEFFER AND MURNA: Ber. **40,** 2007 (1907).
(193) WERTHEIM: J. Am. Chem. Soc. **51,** 3661 (1929).
(194) LARSSON: Z. anal. Chem. **79,** 170 (1929).
(195) KIMBALL, KRAMER AND REID: J. Am. Chem. Soc. **43,** 1199 (1921).
(196) BORGSTROM AND REID: Ind. Eng. Chem. Anal. Ed. **1,** No. 4, 186 (1929).
(197) ZEREWITINOFF: Ber. **41,** 2233 (1908).
(198) BARBER: J. Chem. Soc. **1929,** 1024.
(199) WEBER: Ber. **33,** 795 (footnote) (1900).
(199a) WEEDON AND DOUGHTY: Amer. Chem. J. **33,** 386 (1905).
(199b) GRANDJEAN-HIRTER: Chem. Zentr. **1916,** II, 1181.
(200) DIXON AND TUNNICLIFFE: Proc. Roy. Soc. (London) **94B,** 266 (1923).
(200a) PIGORINI: Arch. farmacol. sper. **10,** 1 (1912).
(200b) NENCKI: Jahresber. Tierchem., p. 193 (1891).
(200c) SIEBERT AND SCHUBENKO: Jahresber. Tierchem., p. 8 (1892).
(200d) HERTER: Chem. Zentr. **1906,** I, 1796.
(200e) BECKMANN: Pharm. Zentralhalle **37,** 557 (1896).
(200f) WILLIAMS AND DRISSEN: J. Biol. Chem. **87,** 441 (1930).
(201) SCHOELLER, FELDT, GEHRKE AND BORGWARDT: U. S. pat. 1,685,341.
(201a) SCHOELLER AND ALLARDT: U. S. pat. 1,689,366.
(201b) British pat. 157,226.
(201c) MEISTER, LUCIUS AND BRUNING: British pat. 157,853.
(201d) MEISTER, LUCIUS AND BRUNING. British pat. 157,266.
(201e) BOURNE: J. Pharmacol. **28,** 409 (1926).
(201f) GERMAN pat. 46,333.
(202) STAUDINGER AND REICHSTEIN: Canadian pat. 283,765.
(202a) INTERN. NÄHRUNGS AND GENUSSMITTEL A.-G.: British pat. 286,152, French pat. 644,137.
(203) British pat. 293,363.

(204) VOTOCEK AND VESELY: Chem. Zentr. **1916,** I, 602.
(205) German pat. 189,200.
(205a) BERNTHSEN: Ann. **251,** 1 (1889).
(205b) FRIEDLÄNDER, MÜLLER AND LASKE: Ann. **351,** 390 (1907).
(205c) FARBWERKE VORM. M. L. AND B.: German pat. 241,985.
(205d) BAYER AND CO.: German pat. 206,536.
(205e) German pat. 208,640.
(205f) BAYER AND CO.: German pat. 116,951.
(205g) HOFFI AND JÖRG: U. S. pat. 1,706,489.
(205h) BAD. ANIL. U. SODAF.: German pat. 175,070.
(205i) I. G. FARBENIND. A. G.: French pat. 662,454.
(205j) HESS AND LEAPER: U. S. pat. 1,729,615.
(205k) I. G. FARBENIND A. G.: French pat. 642,128. British pat. 279,136.
(205l) HÖCHSTER FARBEWERKE: German pat. 228,868 (1910).
(205m) German pat. 45,120.
(205n) German pat. 234,375.
(205o) German pat. 216,269.
(205p) German pat. 198,509.
(205q) French pat. 437,632.
(206) BLUMENSTOCK-HALWARD AND JUSA: Monatsh. **50,** 123 (1928).
(207) I. G.: British pat. 306,492.
(207a) I. G.: French pat. 669,921.
(207b) TEPPEMA AND SEBRELL: Canadian pat. 299,965.
(207c) ROBERTS AND MERKLE: U. S. pat. 1,712,968.
(208) SAYERS AND OTHERS: R. I. 3007, Bureau of Mines (1930).
(209) FISCHER AND ADDAMS: Canadian pat. 278,206.
(209a) BLACK AND LOW: U. S. pat. 1,696,377.
(209b) HILLMANN: British pat. 214,733.
(209c) YOUNG AND PEAKE: Chem. Met. Eng. **27,** 972 (1922).
(209d) DUNSTAN AND BROOKS.: Ind Eng. Chem. **14,** 1112 (1922).
(209e) SCHWARZ AND NEVITT: Petroleum **7,** 23, 96 (1919).
(209f) DUNSTAN, THOLE AND REMFRY: J. Soc. Chem. Ind. **43,** 193 (1924).
(209g) WATERMAN: J. Inst. Petroleum Tech. **10,** 812 (1924).
(209h) STADNIKOV, GAVRILOV AND RAKOVSKII: Brennstoff-Chem. **7,** 65 (1926).
(209i) MORRELL AND FARAGHER: Ind. Eng. Chem. **19,** 1045 (1927).
(209j) WOOD, GREENE AND PROVINE: Ind. Eng. Chem. **18,** 823 (1926).
(209k) HOUNSELL: Nat. Petroleum News, Jan. 4, 1928.
(209l) FULREADER: Ind. Eng. Chem. **21,** 691 (1929).
(209m) DUNSTAN: J. Roy. Soc. Arts **76,** 922 (1928).
(209n) DUNSTAN: Oil Gas J. **27,** No. 42, 169, 175 (1929).
(209o) BIRCH AND NORRIS: Refiner Natural Gasoline Mfg. **7,** No. 7, 94 (1928).
(209p) BLUMENBERG: Canadian pat. 280,816.
(209q) ANGLO-SAXON PETROLEUM CO.: British pat. 214,733.
(209r) DEMOULINS AND JARNES: British pat. 216,918.
(209s) THOLE AND CARD: British pat. 231,944.
(209t) I. G.: British pat. 274,828.
(209u) KIMBALL: British pat. 291,379.
(209v) STAND. OIL DEV. CO.: British pat. 295,728.

(210) COBB: U. S. pat. 1,357,224.
(210a) COBB: U. S. pat. 1,357,225.
(210b) DUNSTAN: U. S. pat. 1,435,824.
(210c) RATHER: U. S. pat. 1,580,531.
(210d) RIDGE AND HODGKINSON: U. S. pat. 1,608,339.
(210e) MORRELL AND COMAY: U. S. pat. 1,627,055.
(210f) WENDT: U. S. pat. 1,658,505.
(210g) CROSS: U. S. pat. 1,654,581.
(210h) WENDT: U. S. pat. 1,668,225.
(210i) HALLETT: U. S. pat. 1,678,984.
(210j) TIJMSTRA: U. S. pat. 1,684,159.
(210k) PHILLIPS AND STAFFORD: U. S. pat. 1,687,992.
(210l) CALDWELL: U. S. pat. 1,691,266.
(210m) IHRIG: U. S. pat. 1,712,619.
(210n) BURWELL AND SHERMAN: U. S. pat. 1,738,656.
(210o) PAULUS: U. S. pat. 1,716,973.
(210p) EGLOFF AND MORRELL: U. S. pat. 1,725,068.
(210q) MORRELL: U. S. pat. 1,733,619.
(210r) BLACK: U. S. pat. 1,749,240.
(210s) BLACK AND MCCONNELL: U. S. pat. 1,759,730.
(210t) ROWSEY: U. S. pat. 1,754,649.
(210u) BORGSTROM: Ind. Eng. Chem. **22,** 249 (1930).
(210v) BORGSTROM, DIETZ AND REID.: Ind. Eng. Chem. **22,** 245 (1930).