ALLOPHANATES[1]

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CONTENTS

I. INTRODUCTION

Allophanates are esters of allophanic acid, $H_2NCONHCOOH$, an acid which is known only in the form of its derivatives. Allophanates may be prepared from primary, secondary, and tertiary alcohols and from phenols. Although as derivatives they have certain advantages over those usually employed for the identification of alcohols, only a partial listing of the reported allophanates has been made (19, 20) and in only one text on qualitative organic analysis known to the authors are these compounds mentioned (33). Only one brief review of the reaction exists in the English language (20).

It was in 1830 that Liebig and Wöhler (129) first reported the isolation of a new compound resulting from the treatment of methanol with cyanic acid. No physical constants nor analytical data were given by them until sixteen years later (130), when they set out the correct formula and analysis. Having been surprised in isolating neither a cyanide, a cyanate, nor a cyanurate, they named the compound an allophanate.[4, 5] Although this is the historical develop-

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[4] Allophane: Greek *allophanes*, "appearing otherwise," from *allos* (otherwise) + *phainesthai* (to appear).

[5] The term has also been used to describe a class of inorganic aluminum silicates. These are not under consideration here. Although α- and γ-substituted allophanates are also known, the discussion has been limited to esters of the unsubstituted acid:

$$(\underset{\gamma}{H_2N}—\underset{\beta}{CO}—\underset{\alpha}{NH}—COOH)$$

ment as usually cited, the work of Richardson (166) and of Schlieper (186) must be considered.

In 1837 Richardson published the first ultimate analysis for an allophanate but gave twice the molecular weight for the empirical formula. Schlieper, in 1846, gave the correct ultimate analysis for the product resulting from passing cyanic acid into fusel oil, probably isoamyl allophanate. Neither the melting point nor the correct formula was given, but several chemical reactions were discussed.

Between 1846 and 1919 new members of this class of compounds and new methods for preparing them were reported, but it remained for Béhal (11) to carry out the first extensive preparative study. Later, Locquin and Sung (135–139), Mastagli (141, 142), and Spielman, Barnes, and Close (194) made important contributions.

The mechanism of the formation of allophanates was first investigated by Hofmann (90) and Davis and Blanchard (43). E. A. Werner and A. E. A. Werner (225 and earlier papers) have most closely studied the reaction of cyanic acid with alcohols.

It is the purpose of this paper to review the known methods of preparation and chemistry of the allophanates, to tabulate the known allophanates with their physical constants, and to present some ideas as to the possible course of future work.

II. FORMATION OF ALLOPHANATES

A. From cyanic acid

The most frequently used procedure for the preparation of allophanates is the reaction of an alcohol with cyanic acid. Cyanuric acid is depolymerized to cyanic acid in a stream of carbon dioxide or nitrogen and passed into the alcohol (23, 84, 95, 129, 130, 165, 194, 210, 219) or into a solution of the alcohol in an inert solvent (108, 222). Alternatively, the cyanic acid may be condensed (b.p. 23.5°C.) into an inert solvent and the alcohol added (89, 106, 150, 173, 174, 181, 185, 191, 205, 221).

$$C_3H_3N_3O_3 \xrightarrow[\text{carbon dioxide or nitrogen}]{>360°C.} 3HNCO$$

$$ROH + 2HNCO \rightarrow \underset{\text{Allophanate}}{ROCONHCONH_2}$$

An apparatus similar to that of figure 1 may be used. The heating wire is conveniently operated from a variable transformer. By using the same length of wire and substituting for B a similar piece of tubing with a T in it for a thermometer, it is possible to determine what setting of the transformer will correspond to 360–400°C. Electrical heating is employed to avoid using a flame near the receiver, which may have in it a volatile solvent, such as ether or benzene.

The alcohol alone, or in a suitable inert solvent, is placed in a test tube or

other receiver at C so that the delivery tube is just below the liquid level. If the delivery tube becomes clogged it may expediently be cleared with a short length of wire. The receiver is cooled in an ice–water mixture. An excess of cyanuric acid is placed in B and a few pieces of dry ice in A, and the apparatus is heated. Cyanic acid is passed into the alcohol or the solution until no further solid separates.

The crude allophanate is filtered, washed with cold ether to remove unreacted alcohol and urethan, and then recrystallized from a suitable solvent. Allophanates have been recrystallized from water, ethanol, methanol, benzene, chloroform, acetone, ethyl ether, and petroleum ether. Water, ethanol, acetone, and benzene have proved adequate in the hands of the authors.

The cyanic acid may also be furnished by treating a cyanate with dry hydrogen chloride in ether (123, 224), by employing a cyanate in acetic acid solution (123), by treating a heavy metal cyanate with hydrogen sulfide (15), or by passing a stream of hydrogen chloride into a suspension of potassium cyanate

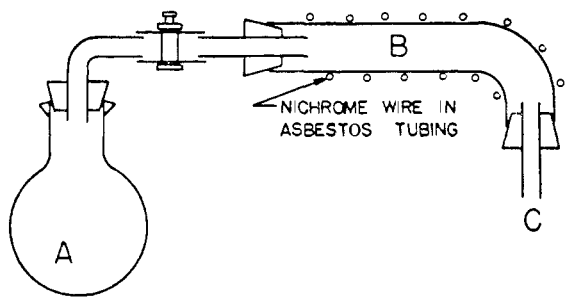


FIG. 1. Apparatus for the preparation of an allophanate from cyanic acid

in alcohol (225). The reaction of cyanic acid on a carbamate has also been reported as giving an allophanate in neutral medium (90, 207) and in acid medium (224).

$$ROCONH_2 + HNCO \xrightarrow{HCl} ROCONHCONH_2$$

Saytzeff (176, 177) reported that in the reaction of potassium cyanate with ethyl chloroacetate in 90 per cent ethanol solution two allophanates were obtained—ethyl and carbethoxymethyl allophanates.

$$2KNCO + C_2H_5OH \rightarrow C_2H_5OCONHCONH_2 + 2KOH$$

Ethyl allophanate

$$2KNCO + ClCH_2COOC_2H_5 \rightarrow C_2H_5OCOCH_2NHCONH_2 + KCl + KOH$$

Carbethoxymethyl allophanate

Amato (1, 2) reported a similar experience somewhat later. Another reaction in which potassium cyanate figures as the source of cyanic acid was reported by Wilm (231). Refluxing a solution of the salt with ethyl chloroformate in absolute

ethanol gave potassium carbonate and potassium chloride, ethyl allophanate, ethyl carbonate, and a small quantity of cyanuric acid.

$$2C_2H_5OCOCl + 2KNCO + 3C_2H_5OH \rightarrow$$

$$C_2H_5OCONHCONH_2 + 2KCl + 2(C_2H_5)_2CO_3$$

Ethyl allophanate

Another source of cyanic acid is the decomposition of urea in the presence of an alcohol (30, 90, 93, 236).

$$H_2NCONH_2 \rightleftarrows HNCO + NH_3$$

$$ROH + 2HNCO \rightarrow ROCONHCONH_2$$

B. From certain acid chlorides

A second general procedure for the preparation of allophanates is by the treatment of an alcohol with an acid chloride. Carbamyl chloride may be used with the alcohol (70, 146, 190, 210, 231, 234)

$$ROH + 2H_2NCOCl \rightarrow ROCONHCONH_2 + 2HCl$$

or allophanyl chloride either in pyridine (46, 47, 158) or without pyridine (23, 82, 83, 150, 152, 154, 158).

$$ROH + H_2NCONHCOCl \rightarrow ROCONHCONH_2 + HCl$$

In the absence of pyridine the reaction of allophanyl chloride with an unsaturated alcohol was reported to give addition of hydrogen chloride across the double bond (150) and in one instance the tertiary hydroxyl was replaced by chlorine in a dihydroxy compound (158). In the latter case, the reaction proceeded normally in pyridine to give a diallophanate.

Urea may be acylated to produce an allophanate. Thus, ethyl chloroformate (41, 180, 232) and 3-chloropropyl chloroformate (58) give the corresponding allophanates upon reaction with urea.

$$ROCOCl + H_2NCONH_2 \rightarrow ROCONHCONH_2 + HCl$$

The reaction appears to give better yields in the presence of an excess of urea, which takes up the acid formed (180).

C. From carbamates

In 1886 Loeb (139) first reported that phosgene would react with ethyl carbamate to give an allophanate.

$$2C_2H_5OCONH_2 \xrightarrow[COCl_2]{75°C., \text{ in benzene}} C_2H_5OCONHCONH_2 + C_2H_5OH$$

Ethyl allophanate

Later, thionyl chloride (68, 163, 187, 218, 224), sulfuryl chloride (60), and phosphorus pentoxide (14) were found capable of carrying out the conversion.

$$2ROCONH_2 + SOCl_2 \rightarrow ROCONHCONH_2 + SO_2 + RCl + HCl$$

$$2ROCONH_2 \xrightarrow{SOCl_2,\ <70°C.} ROCONHCONH_2 + ROH$$

$$2ROCONH_2 \xrightarrow{P_2O_5} ROCONHCONH_2 + ROH$$

Phosphorus trichloride and phosphorus oxychloride do not react with urethan in the same way (187).

D. By ammonolysis or hydrolysis

A number of examples exist in which simpler compounds add ammonia or water to give an allophanate, or more complex molecules are ammonolyzed or hydrolyzed to give an allophanate. Thus, carbethoxy isocyanate gives the allophanate with ammonia (55),

$$C_2H_5OCONCO + NH_3 \rightarrow \underset{\text{Ethyl allophanate}}{C_2H_5OCONHCONH_2}$$

carbethoxy cyanamide gives ethyl allophanate with water (145),

$$C_2H_5OCONHCN + H_2O \rightarrow \underset{\text{Ethyl allophanate}}{C_2H_5OCONHCONH_2}$$

and triacylamides are ammonolyzed to the allophanate (52, 54),

$$N(COOR)_3 + NH_3 \rightarrow ROCONHCONH_2 + ROCONH_2 + ROH$$

while dicarbethoxy cyanamide may be selectively hydrolyzed to give, in one case, an allophanate (53).

$$(C_2H_5OCO)_2NCN + H_2O \xrightarrow{\text{concentrated acid}} (C_2H_5OCO)_2NCONH_2$$

$$\underset{\substack{\text{Dicarbethoxy}\\ \text{cyanamide}}}{(C_2H_5OCO)_2NCN} + H_2O \xrightarrow{\text{dilute acid}} \underset{\text{Ethyl allophanate}}{C_2H_5OCONHCONH_2} + C_2H_5OH + CO_2$$

Urea appears to be the ammonolytic reagent with ethyl oxalate (86), oxamide and ethyl allophanate being formed (see later).

$$\underset{\text{Ethyl oxalate}}{C_2H_5OCOCOOC_2H_5} + H_2NCONH_2 \xrightarrow{125°C.,\ \text{sealed tube}} \underset{\text{Oxamide}}{H_2NCOCONH_2} + C_2H_5OH + \underset{\text{Ethyl allophanate}}{C_2H_5OCONH_2CONH_2}$$

The hydrolysis or ammonolysis of more complex ureides is shown in the following equations:

$$OC(NHCOOC_2H_5)_2 + H_2O \rightarrow \underset{\text{Ethyl allophanate}}{C_2H_5OCONHCONH_2} + CO_2 + C_2H_5OH \quad (40)$$

$$C_2H_5OCONHCOCOOK + RNH_2 \rightarrow C_2H_5OCONHCONH_2 + RNHCOCOOK \quad (140)$$

$$C_2H_5OCONHCONHCOCOOK + H_2O \xrightarrow{\text{boil for short time}} C_2H_5OCONHCONH_2 + KHC_2O_4 \quad (143)$$

E. By miscellaneous methods

The electrolysis of formamide in ethanol is reported to give a "good yield" of the allophanate (179). Benzyl alcohol gives only meager yields, while polyhydroxy alcohols fail to give the allophanates. During an investigation of the rearrangement of potassium glycolobenzoylhydroxamate in boiling isoamyl alcohol, isoamyl allophanate was isolated (91). The reaction of α-diazotoluene with ethyl nitrocarbamate afforded a small quantity of benzyl allophanate (73). Linhard (131) claims that when carbamidosulfonic acid is added directly to ethanol a mixture of the carbamate and the allophanate is formed.

$$\underset{\text{Carbamido-sulfonic acid}}{H_2NCONHSO_3H} + C_2H_5OH \rightarrow \underset{\text{Ethyl allophanate}}{C_2H_5OCONHCONH_2} + 2C_2H_5(NH_4)SO_4$$

Azides have been shown to give allophanates (38, 39).

$$C_2H_5OH + H_2NCOCON_3 \xrightarrow{\text{reflux}} C_2H_5OCONHCONH_2 + N_2$$

$$C_6H_5CHOHNHCOOC_2H_5 + C_6H_5CHOHCON_3 \rightarrow 2C_6H_5CHO + C_2H_5OCONHCONH_2 + N_2$$

Métayer (147) has reported that distillation of a urethan, especially in the presence of Raney nickel, will give an allophanate. Davis and Blanchard (42) and Bishop (16) have reported that while nitrobiuret may be refluxed with absolute ethyl, propyl, butyl, and *tert*-butyl alcohols without reaction and likewise with the addition of 1 per cent of water, the allophanates are formed when more water is added. Most recently, Böttcher and Bauer (22) have reported that the pyrolysis of aryl diurethans can give an allophanate along with some carbamate and cyanuric acid.

$$C_2H_5OCONHCH(Ar)NHCOOC_2H_5 \xrightarrow{125\text{–}300^\circ C.} C_2H_5OCONHCONH_2$$

Adelson (237, 238) has reported that allophanates may be prepared in improved yields when an alcohol and biuret are heated at reduced pressures.

F. Scope and limitations of the methods

Cyanic acid may be used directly to prepare the allophanates of primary, secondary, and tertiary alcohols, glycols, and phenols. Ethylene glycol and glycerol give monoallophanates (4). Because of the greater ease of hydrolysis of

aryl allophanates, these are most often made through use of carbamyl chloride or allophanyl chloride. For forming derivatives of small quantities of phenol the cyanic acid procedure is satisfactory, although some carbamate may also be present. An interesting synthesis is the preparation of the allophanate of 1,2,2,2-tetrachloroethanol by treating chloral with carbamyl chloride (212).

Carbamyl chloride and allophanyl chloride may be considered as forcing reagents; the yields of allophanates are generally better than with cyanic acid. These chlorides are preferred reagents for the reaction with phenols and thiophenols (128). As implied earlier, a base should be present to take up hydrogen chloride formed in the reaction to prevent further reaction at other sites in the molecule; for example, at a double bond by addition or at a tertiary alcohol by replacement.

Werner (224) claims that the highest yields of allophanate are achieved by means of the action of thionyl chloride on the corresponding carbamate. This method was tested for ethyl, isopropyl, butyl, and isoamyl allophanates. Since this procedure requires the prior preparation of the carbamate, it is difficult to recommend it as advantageous over the use of carbamyl chloride or allophanyl chloride directly on the alcohol.

Some disadvantages in the use of allophanates as derivatives of alcohols should be noted. The yields are often low. With alcohols such as $C_6H_5CH(R)OH$ only about 20 per cent yields have been obtained, using cyanic acid obtained by the pyrolysis of cyanuric acid. In preliminary experiments even lower yields have been obtained with other methods: namely, (*a*) carbinol and urea, (*b*) carbinol and potassium cyanate in the presence of acid, (*c*) carbinol and biuret, (*d*) chlorocarbonate and urea, (*e*) carbamate and thionyl chloride, and (*f*) carbamate and thionyl chloride and urea (34). Among the alcohols which give poor yields of the allophanates are 1-phenylethanol, 1-phenyl-1-propanol, 1-(*sec*-amyl)-1-propanol, allyldimethylmethanol, and cyclopropylphenylmethanol.

Another point is that the melting points are not always as unequivocal as desired. Close has supplied the fact that certain allophanates do not show the expected depression when mixed melting points are determined, as shown by the following example (34):

	Melting point °C.
tert-Amyl allophanate	168–169 (gas)
1-Ethylpropyl allophanate	175–176 (gas)
Mixture	171–172 (gas)

There is reason to believe that decomposition occurs with melting more frequently than has been reported.

The use of cyanic acid permits the formation of derivatives of a wide variety of substituted alcohols. Among the functional groups which do not appear to interfere with allophanate formation are double bonds, triple bonds, conjugated systems, halogens, ethers, quaternary nitrogen atoms, sulfide links, carbonyl groups, ester groups, and carboxyl groups.

One question which has not been answered is the following: "Can cyanic acid ($K_a = 2.2 \times 10^{-4}$ at room temperature (122)) cause the rearrangement of alcohols such as the allyl and propargyl alcohols and the *i*-steroids?"

III. MECHANISM OF THE REACTIONS LEADING TO ALLOPHANATES

The first studies on the mechanism of the reaction of cyanic acid with an alcohol to produce an allophanate were made by Hofmann (90). He stated that when an allophanate is prepared, the urethan is formed when the alcohol is in excess and the allophanate when the cyanic acid is in excess. The evidence offered was that a mixture of amyl allophanate and amyl alcohol in a sealed tube at 160–180°C. gave some amyl urethan, thus marking the urethan as the intermediate between the alcohol and the allophanate.

$$ROH + HNCO \rightarrow ROCONH_2$$

$$ROCONH_2 + NHCO \rightarrow ROCONHCONH_2$$

Eighteen years later, in 1889, Traube (207) reported that when benzyl carbamate was treated with cyanic acid, benzyl allophanate was formed. Further, he claimed that when 1 mole of allophanate was heated with 1 mole of alcohol, 2 moles of urethan were formed. These findings essentially corroborated those of Hofmann.

In 1929 Davis and Blanchard (43) reported on the inability to reproduce the results of Hofmann and proposed a novel course for the reaction.[6] On the basis of the following evidence they postulated a non-isolable compound as the reactive allophanate-former. In aqueous solution cyanic acid ionizes as a weak acid, trimerizes to cyanuric acid, hydrolyzes to ammonia and carbon dioxide, thus forming ammonium cyanate, and finally dimerizes to dicyanic acid. The last compound can react with aniline to give phenylbiuret or with an alcohol to give an allophanate. It cannot, however, be isolated from aqueous solution, because it undergoes either depolymerization or hydrolysis during evaporation of the solvent. Further evidence cited was that when urea and 1-butanol are refluxed for 3 hr., the allophanate and carbamate are formed and less allophanate is present at the end of 6 hr. Also, 1-butanol and biuret gave a mixture of allophanate and carbamate with less allophanate at longer times. Thus, the dicyanic acid is presumed to form directly and independently of the carbamate as shown below:

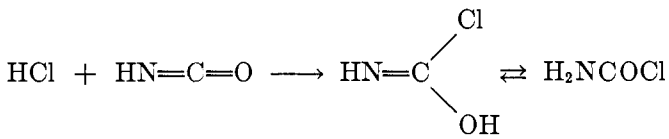
$$2HNCO \rightleftarrows O{=}C{=}NCONH_2$$

$$ROH + O{=}C{=}NCONH_2 \rightarrow ROCONHCONH_2$$

In a series of papers A. E. A. Werner and coworkers (207, 225, 228) have refuted the work of Davis and Blanchard and also the work of Hofmann and Traube. Specifically, they were unable to duplicate the synthesis of ethyl allo-

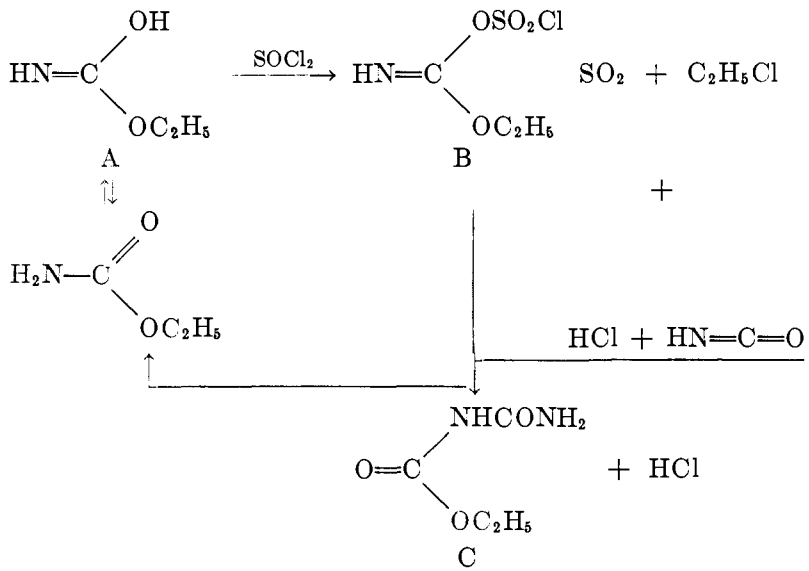
[6] It is curious that Davis and Blanchard (43) report that Béhal (11) was also unable to reproduce the work of Hofmann, but there is no record in reference 10 of any attempt to check Hofmann's work.

phanate by passing cyanic acid into molten ethyl carbamate or into a neutral solution of urethan in ether. Likewise, this conversion failed when they treated urethan with a mixture of finely ground potassium cyanate and acetic acid. Also, when urea and urethan were heated at 145–170°C. for 3 hr., only unchanged urethan, biuret, and cyanuric acid were recovered, with no trace of allophanate. However, the allophanate was readily prepared when the cyanic acid was produced in the presence of hydrogen chloride. Addition of potassium, sodium, or silver cyanate to a solution of urethan in anhydrous ether saturated with dry hydrogen chloride at room temperature gave the allophanate in about 70 per cent yield. Benzene or dioxane could also be used as the solvent. Werner and Gray (207) claim that the direct addition of cyanic acid to the carbonamide group—$CONH_2$—is brought about when the cyanic acid is liberated in the presence of hydrogen chloride, because a nascent carbamyl chloride is formed *in situ*.

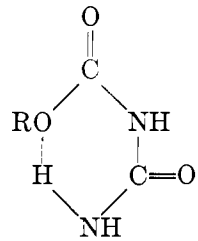


The nascent carbamyl chloride then converts the carbamate to the allophanate. This intermediate is the one actually used by Gattermann (70) to convert ethanol to ethyl allophanate and also the one which he postulated as giving aromatic amides from aromatic hydrocarbons in the reaction now bearing his name.

Finally, by combining their observations with the work of Raiford and Freyermuth (164), the Werners wrote the mechanism for the conversion of ethyl carbamate to ethyl allophanate as follows:



An interesting question is why the reaction with cyanic acid stops when two molecules have been added per molecule of alcohol. A. E. A. Werner (226) postulated that in the hydrolysis of diacylureas the formation of a six-membered chelate ring halted the hydrolysis at the removal of one acyl group. This concept may be applied to show that at the formation of a chelated six-membered ring the allophanate is stabilized.



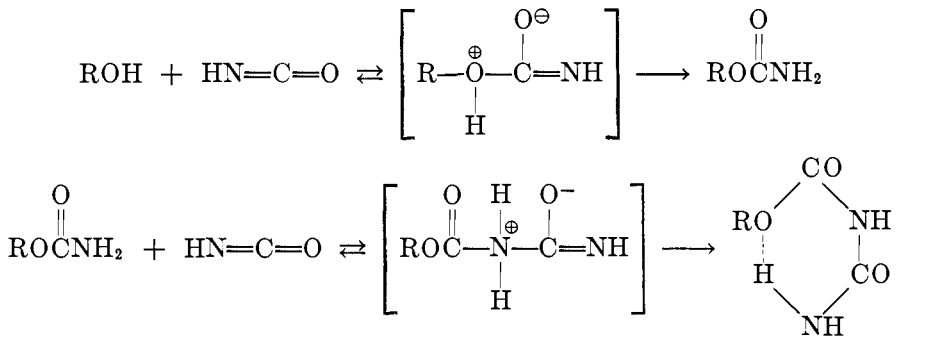
Johnson and Ferstandig (101) claim that they have clearly elucidated the mechanism of this reaction, but their work has not yet appeared in print.

Certain conflicting experiments reported in the literature still remain unanswered. Even facts obtained by Cahours (30), Hofmann (90), Lane (123), and Traube (207) seem to refute parts of the mechanistic picture described by the Werners. Lane (123), for example, claims to have converted 2-methoxy-, 2-ethoxy-, 2-butoxy-, 2-phenoxy-, and 2,2′-butoxyethoxyethanols to the corresponding allophanates by treating the alcohols with suspensions of sodium cyanate in acetic acid, a reaction which the Werners claim does not work.

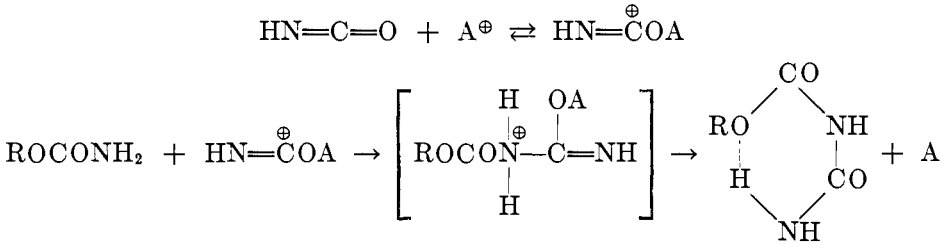
Birckenbach and Kolb (15) have reported that cyanic acid obtained by treating silver or mercuric cyanate with hydrogen sulfide or with hydrogen chloride in methanol gives only methyl urethan. The cyanic acid obtained by isolation and distillation and then addition to methanol gives urethan and allophanate. Further, the cyanic acid obtained from double decomposition of potassium cyanate, mercuric cyanate mixed with potassium salts, silver cyanate plus alkali metal salts, lead cyanate, and tetramethylammonium cyanate always gives allophanate, with occasionally some urethan. The authors emphasized that a urethan cannot be converted directly to the corresponding allophanate by subsequent addition of cyanic acid. Without further evidence the authors claimed that their results also supported the dicyanic acid postulate of Davis and Blanchard.

One factor which has not been investigated nor mentioned in any of the papers in the field is the purity of the cyanuric acid taken for depolymerization to cyanic acid. It is well known that when zinc chloride is heated with urea it gives cyanuric acid. Since the product is purified by extraction with water, it is doubtful that all of the zinc chloride is removed. During depolymerization of the cyanuric acid small quantities of residual zinc chloride may be volatilized into the stream of carbon dioxide and carried into the reaction mixture. If the reaction between an alcohol and cyanic acid is considered in the modern view as proceeding in two steps, the following equations may be written:[7]

[7] See references 131–134, inclusive, for evidence that cyanic acid normally is HNCO rather than HOCN.



In the first step a pair of electrons on oxygen attacks the carbon atom of cyanic acid to give the unstable intermediate, which rearranges to the stable carbamate. In the second step, a pair of electrons on the amide nitrogen must attack the carbon of a second molecule of cyanic acid in advance of rearrangement to the allophanate. It is probable that, in the amide, the electrons on nitrogen are not as available for nucleophilic displacement as in an alcohol. This, then, is the slow step. Slight differences in basicity of the alcohols may account for the ease of conversion directly to the allophanate. This may be depicted as follows:



Zinc chloride as well as hydrogen chloride may serve as the Lewis acid A. To establish this hypothesis, it would be necessary to study the effect on the course of the reaction of a number of salts capable of acting as Lewis acids. It would be desirable to study the rate of formation of carbamate and of allophanate as a function of acid strength. It may thus be possible to demonstrate that cyanic acid ($K_a = 2.2 \times 10^{-4}$) at room temperature is capable of catalyzing the conversion of most alcohols to the carbamate but only of certain alcohols to the allophanates.

IV. PROPERTIES AND REACTIONS OF ALLOPHANATES

The chemistry of allophanates has been little studied. Hydrolysis, salt formation, ammonolysis, pyrolysis, reaction with thionyl chloride, acylation, and reaction with halogens have been tried and will be discussed in that order in this section.

The hydrolysis of allophanates may be effected readily by warm alkalies (4, 29, 118, 130, 171, 186). After purification and saponification, the pure alcohol and water-soluble products are obtained—an excellent way in which to purify an

alcohol. Rovira (171) found that potassium benzylate could be used to decompose and analyze the allophanates, since it led to the quantitative evolution of ammonia, which may be absorbed in standard sulfuric acid and titrated. Cold alkalies decompose the allophanates also, but only slowly, so that it is possible to reprecipitate the allophanates from the alkaline solutions if the solutions are neutralized promptly (60, 143). Baeyer (4) reported that with potassium hydroxide, potassium carbonate formed and no potassium allophanate was obtained. Lane (124) has patented the use of allophanates as a means for modifying cellulose fabrics and claims that they are not destroyed by hot alkaline soap solutions. This statement is in contrast to much previous work.

Even in neutral solution allophanates may be hydrolyzed, but this requires an elevated temperature (160°C.) beyond that found in crystallization from the usual solvents (90). Phenolic allophanates, on the other hand, are hydrolyzed by boiling water (24).

Concentrated sulfuric or nitric acid decomposes glyceryl allophanate (a monoallophanate) with the evolution of carbon dioxide, a reaction which was interpreted as hydrolysis (4). However, cold dilute acids did not affect this allophanate.

Salts of allophanates have been prepared by the reaction of bases with ethyl allophanate (18, 60, 130, 176, 208). In this way, the barium (130, 176), calcium (130), potassium (130, 143), and sodium (60, 130) salts have been prepared. The sodium salt has also been prepared by double decomposition of the barium salt with sodium sulfate (130). The potassium salt has been obtained by adding ethyl allophanate to a solution of potassium amide in liquid ammonia (18). The disilver salt has been precipitated by treating ethyl allophanate with silver nitrate in hot water (40). It is not entirely surprising that treatment of the barium salt with neutral silver oxide or lead acetate failed to precipitate the new metal salt (130). It is interesting to note that a disodium salt of allophanic acid has been isolated by treating ethyl carbamate with sodium in benzene (60).

The acidity of the allophanates appears to arise from the diacyl nitrogen structure, $ROCONHCONH_2$, which is well known to be responsible for the acidity of barbiturates and other classes of compounds.

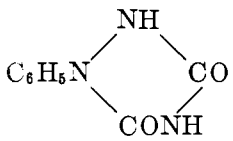
Apparently acids can also form salts with allophanates. Mauquin (143) has reported that treatment of ethyl allophanate with nitric acid in ether gave beautiful crystals of the mononitrate.

Ammonolyses of allophanates have been effected with ammonia (17, 90, 207), aromatic amines (41, 90), aliphatic amines (90), and phenylhydrazine (41). Blair (17) reported that at 300°C. a mixture of ammonia, ammonium chloride, and ethyl allophanate produced a mixture of guanidine, urea, and ammonium carbamate, while at lower temperatures ammonia alone with ethyl or methyl allophanate gave biuret and ethanol. Hofmann (90) and Traube (207) also reported that heating with ammonia gave biuret. However, Schlieper (186) reports that ammonia does not react in warm solution.

Aniline at 120–125°C. has been shown to convert ethyl allophanate to diphenylbiuret, while at 160–170°C. it gives a mixture of monophenylurea and

diphenylurea (41). With *o*-anisidine, *o*-toluidine, and *m*-nitroaniline at about 125°C. the products were aryl-substituted allophanates, $ArNHCONHCOOC_2H_5$. As the temperature was raised, substituted biurets and arylureas were formed (41). With aniline, *m*-toluidine, and *p*-bromoaniline, none of the substituted allophanates were obtained; only substituted ureas and biurets were isolated. No explanation for this change in the course of the reaction was offered.

In 1920 Dains and Wertheim (41) showed that when phenylhydrazine reacts with methyl allophanate for a long time at 150°C., 1-phenylurazole is the product.



1-Phenylurazole

Pyrolysis of an allophanate yields the alcohol and cyanuric acid (78, 228). When ethyl allophanate is refluxed with thionyl chloride at atmospheric pressure it is unchanged, but when heated in a sealed tube with xylene at 140–150°C., 5 g. of ethyl allophanate is converted to 2 g. of cyanuric acid (187).

Waltmann and Wolf (217) have reported that stearyl allophanate may be treated with trioxymethylene and dry hydrogen chloride to give a chloromethyl derivative which may then be treated with pyridine at room temperature to give the quaternary salt.

Mauquin (143) has successfully acylated ethyl allophanate with the acid chloride of monoethyl oxalate.

Schlieper (186) has found that a warm aqueous suspension of amyl allophanate does not react with ammonia, nitric acid, chlorine, bromine, or sulfuric acid.

V. USES OF ALLOPHANATES AND FUTURE PROBLEMS

In addition to their application for the identification of alcohols, the allophanates may be used for their purification. As has been stated earlier, allophanates are readily hydrolyzed in acidic or basic solution.

In the patent literature claims have been made for the use of allophanates as intermediates in the preparation of water-repellent fabrics (124, 217), as softeners for hard deposits of carbon on the pistons of engines (61, 239), as additives to lubricants for use at extreme pressures (237, 238), for the conversion of medicinal agents of unpleasant odor or taste to odorless and tasteless compounds (153, 211, 212), and as depilatories (51).

Recently the investigation of allophanates as anticonvulsant drugs was reported (194). Benzyl allophanate, α-ethylbenzyl allophanate, and a few branched-chain aliphatic allophanates were found to be effective against electroshock,

metrazol, or both, but none was deemed worthy of clinical investigation. They were also found to have sleep-producing action.

In respect to the preparation of allophanates, the toxicity of cyanic acid should be mentioned; it is a corrosive liquid at 0°C. Sodium cyanate has a hypnotic action (188).

The discussion of the mechanism of the formation of allophanates makes it clear that additional work needs to be done to complete the picture. However, certain other studies are also obviously lacking.

A quantitative knowledge of the acidity of allophanates is not available. Such data would be of interest in studies of salt formation and in a study of the mechanism of the formation of allophanates as well. Although the allophanates presumably have one acidic hydrogen, only one reaction for their acylation has been carried out (143). The site of acylation was claimed to be the β-position, whereas it would appear that the α-position should carry the more active nitrogen. No alkylation reactions with reagents such as diazomethane[8] and dimethyl sulfate have been reported. The reactions with nitrous acid or with coupling reagents, which conceivably could give interesting if not also useful compounds, have not been studied.

VI. TABLES OF ALLOPHANATES

Table 1 contains data on the allophanates of alcohols which are liquid at 25°C., while table 2 presents data on the allophanates of alcohols which are solid at this temperature. In each table the alcohols are arranged in the order of increasing boiling point. Table 3 contains data on the allophanates of a number of alcohols for which no physical constants are given in the literature. Tables 4 and 5 present data on the allophanates of phenols. Allophanates of a few miscellaneous alcohols are to be found in table 6.

[8] Close (34) has stated that ethyl, isopropyl, and 1-phenylpropyl allophanates fail to react with diazomethane even in the presence of methanol.

TABLE 1

Allophanates of alcohols which are liquid at 25°C.

ALCOHOL	BOILING POINT	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	°C.	
Methanol	65	208	(70)
		210	(224)
		212	(11)
1,1,1-Trifluoro-2-propanol	77.7–77.9	159.7 (dec.)	(200)
Ethanol	78	188	(218)
		190	(11, 39)
		191	(38)
		193	(225)
		194	(140)
		195	(23)
		197–198	(237)
tert-Butyl alcohol	83	190	(11, 194, 237)
2-Propanol	88	179	(224)
		180	(11)
		184–185	(194)
3-Buten-2-ol	96–97	151–152	(44)
Allyl alcohol	97	165	(11, 237)
1-Propanol	98	167	(7)
		169.6–169.8	(92)
		175	(224)
		175.5	(11)
2-Butanol	100	159.5	(11, 194)
2-Methyl-2-butanol	102	151–152[a]	(11, 165)
		166–168	(194)
Cyclopropanol	100–103	179–181 (subliming with decomposition)	(194)
	53–55/100 mm.		
Isobutyl alcohol	107–108	174	(93)
		178–179	(165)
		179–180	(194)
		180.5	(11)
3-Methyl-2-butanol	111.5–112	163[a]	(21)
		169–170	(194)
3-Penten-2-ol	112	158–159	(49)
3-Methyl-3-buten-2-ol	112–113	150–151	(126)
1-Penten-3-ol	114–116	151–152	(45)
		152–153	(44)
		155	(78)
3-Pentanol	116	171–172	(194)
		179.5	(11)
1-Butanol	117	149, 149–150	(224, 164)
		149.5–150.5	(11)
2-Pentanol	119	154	(11)
		157–158	(194)

TABLE 1—*Continued*

ALCOHOL	BOILING POINT	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	°C.	
2-Methyl-2-pentanol	123	125.6–126.6	(125)
		128	(11)
3-Methyl-3-pentanol	123	152	(78)
		153–154	(194)
2-Methoxyethanol	125	163	(123)
2-Methyl-3-pentanol	128	179[b]	(11)
		185–186	(194)
2-Methyl-1-butanol	128	149–150	(194)
2-Chloro-1-ethanol	129	179–182	(194)
		182.5	(78)
3-Methyl-1-butanol	131.5	149.4–150	(92)
		150	(11)
		160	(224)
		162	(7)
4-Methyl-2-pentanol	132	161[b]	(11)
		162–163	(194)
2,4-Dimethyl-2-pentanol	132–133	132	(11)
3,4-Dimethyl-1-pentyn-3-ol	133	144	(127)
1-Hexen-4-ol	76–77.8/95 mm.	169	(67)
1-Hexen-3-ol	133.5–134	139.5–140	(44)
2-Hexen-1-ol	101.4–101.8/95 mm.	154.5–155.5	(66)
4-Ethoxyethanol	135	143–145	(123)
3-Hexanol	135	185.5	(78)
1-Methylcyclopentanol	135–136	157	(32)
3-Ethyl-1-pentyn-3-ol	135–137	130–131	(138)
3-Methyl-1-hexyn-3-ol	137	133	(139)
2-Hexanol	137–138	170–171	(194)
		173[b]	(11)
1-Pentanol	138	158–159	(194)
		159.3–159.8	(92)
		162	(90, 187)
2,4-Dimethyl-3-pentanol	138	173.5–174.5	(21)
3-Methyl-5-hexen-3-ol	139	132–135	(194)
4-Penten-1-ol	138.5–139.5	147–148 (dec.)	(159, 160)
Cyclopentanol	139–140	179.5	(11)
3-Methyl-3-hexanol	140	148	(78)
		149	(235)
2-Penten-1-ol	141–142	157–157.5	(45)
3-Ethyl-3-pentanol	142	156	(78)
		173–174	(194)
		182–183	(144)
3,4,4-Trimethyl-1-pentyn-3-ol	142–144	156	(135)
Methylpseudobutylvinylcarbinol	146–147	167–168	(136)
2-Ethyl-1-butanol	147.7	156–158	(194)
		161–161.5	(21)

TABLE 1—*Continued*

ALCOHOL	BOILING POINT	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	°C.	
2-Methyl-1-pentanol	147.7	150–151	(194)
		155.8–156.6[c]	(125)
5-Methyl-3-hexanol	147–148	185–187	(194)
3,5-Dimethyl-1-hexyn-3-ol	148	114	(127)
cis-o-Methylcyclopentanol	148–149	174	(77)
4-Methyl-3-hexanol	149–150	172–174	(194)
Ethyl α-hydroxyisobutyrate	150	125–126 (dec.)	(194)
trans-o-Methylcyclopentanol	150–151	174	(77)
Trichloroethanol	151	182–183	(230)
4-Methyl-1-pentanol	151–152	155–156	(185)
		162	(11)
2,2,3-Trimethyl-3-pentanol	152	134–135	(135)
3-Heptanol	156	185.4–185.6	(125)
		187	(78)
1-Hepten-3-ol	153.5–154	156.5–157	(44)
4-Heptanol	154–155	206	(11)
2-Ethyl-2-methyl-1-butanol	155	102	(64)
Ethyl lactate	155	170	(207)
1-Hexanol	156	159–160	(147)
		163.3–163.8	(125)
		165	(11)
3-Hexen-1-ol	156–157	143–144 (synthetic)	(174, 204)
		134–135 (natural)	(174)
		143 (*cis*)	(203)
		146 (*trans*)	(203)
		146 (natural)	(204)
2,4-Dimethylpentanol	157	116–117	(194)
4-Hexen-1-ol	155–158	161.5	(167, 168)
2-Heptanol	158–160	148–150	(19, 194)
Ethyl glycolate	160	144	(207)
3-Ethyl-3-hexanol	161	149	(11)
3-Chloro-1-propanol	160–162	166	(58)
1,1,1-Trichloro-2-propanol	161	186	(212)
Cyclohexanol	161	173	(194)
		179	(11)
2-Diethylaminoethanol	162	137–138	(146)
3-Methyl-3-heptanol	164	130	(78)
2-Methylcyclohexanol	166.5	177	(78)
Furfuryl alcohol	170	167.5[a]	(78)
2-Butoxyethanol	171	118	(123)
3,5-Dimethyl-4-heptanol	171	163	(209)

TABLE 1—*Continued*

ALCOHOL	BOILING POINT	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	°C.	
cis-3-Methylcyclohexanol	171–171.4	141.6	(121)
3-Ethyl-5-methyl-3-hexanol	172	145	(11)
3-Methyl-1-hexanol	172	137	(235)
trans-3-Methylcyclohexanol	173.6–174.6	178.8	(121)
cis-1,4-Dimethyl-2-cyclohexanol	175	158[d]	(74, 75)
cis-1,3-Dimethylcyclohexan-*trans*-4-ol	175–176	207[d]	(76)
cis-1,3-Dimethylcyclohexan-*cis*-4-ol	176	184[d]	(76)
1-Heptanol	176	160	(11)
1,3-Dimethyl-4-cyclohexanol	176–177	149[d]	(76)
trans-1,4-Dimethyl-2-cyclohexanol	177	125[d]	(74, 75)
2-Methyl-2-hepten-6-ol	177–178	99–100	(56)
1,3-Dichloro-2-propanol	178	182	(190)
Tetrahydrofurfuryl alcohol	178	161–161.5[e]	(92)
2,6-Dimethyl-4-heptanol	178	156[b]	(11)
2-Octanol	179	155	(11)
3-Octanol	178.5–179.5	167	(12)
d-3-Octanol	88–92/33 mm.	182	(29)
2-Hydroxyethyl formate	179–180	151	(83)
3-Methyl-4-octanol	180	160	(209)
4-Ethyl-4-heptanol	180	124	(135)
2-Ethyl-1-hexanol	181–183	124	(147)
		125	(142)
Cycloheptanol	185	184	(173)
3,7-Dimethyl-1-octyn-3-ol	187–188	114–115	(135)
2-Hydroxyethyl acetate	187–189	164	(83)
3,5,5-Trimethyl-1-hexanol	191	148.5–149	(21)
5-Nonanol	194	158	(209)
2,2'-Ethoxyethoxyethanol	195	102–104	(123)
1-Octanol	194–196	155–156	(70)
		157	(11)
Ethylene glycol	197	153.8–154.8	(92)
		160	(4, 237)
1-Phenylethanol	204	181–182	(193)
		181.5	(11)
		185–186	(194)
Benzyl alcohol	206	121	(11)
		182–183	(194)
		183	(207)
		191.5	(23)
		191–191.5	(152)
1-Nonanol	211	158	(11)
d-Neomenthol	211.5–211.8	215.5	(236)
α-Allyl-α-methylbenzyl alcohol	217–221	139–143 (dec.)	(194)
1-Phenyl-1-propanol	217–221	149–150	(194)
Phenethyl alcohol	219–221	186	(11)
		197.5	(23)

TABLE 1—*Continued*

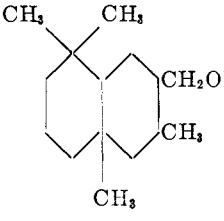
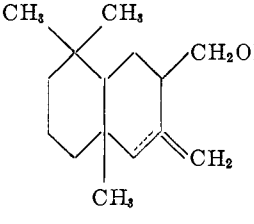
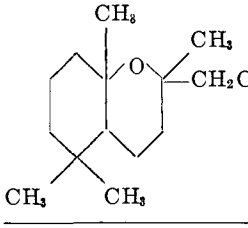
ALCOHOL	BOILING POINT	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	°C.	
Carvomenthol	222	192.5	(11)
3-Phenyl-3-pentanol	223–224	151–152	(194)
Nerol	224–225	84–84.5	(152)
Undecanol	225.4	155.5–158	(11)
Geraniol	229	120–121	(25, 184)
		124–124.5	(149, 152, 237)
2,2'-Butoxyethoxyethanol	230.4	88	(123)
1-Decanol	233	159	(11)
Phenylpropanol	236	165	(11)
2-Phenoxyethanol	237	123	(82)
		219–220	(123)
Cinnamyl alcohol	258	185	(11, 237)
1-Dodecanol	259	159	(97)
		159.5	(11)
Anisyl alcohol	259	180.25	(11)
Diethyl tartrate	280	188	(207)
Glycerol	290	About 160	(4)
2,3-Dimethyl-1-penten-3-ol	44–45/18 mm.	147	(36)
1,10-Dimethyl-5,10-*cis*-7-naphthiten-1-ol	77–78/0.3 mm.	178.8–179.6 (dec.)	(69)
3,6,7-Trimethyl-2,6-octadien-8-ol	61–62/0.009 mm.	108–109	(182)
2-(2',6',6'-Trimethyltetrahydro-2'-pyranyl)ethanol	62–63/0.2 mm.	165–165.5	(31)
2-Hydroxymethyl-5,5-dimethylcyclohexanone	66/0.24 mm.	154	(197)
	95–96/0.05 mm.	162–163	(35)
	98–100/0.05 mm.	183–185 (not constant)	(35)
	104–105/0.05 mm.	167	(31)

TABLE 1—*Continued*

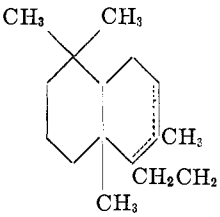
ALCOHOL	BOILING POINT	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	°C.	
Phytol	155–157/1 mm.	74[f]	(116)
		77–78	(206)
Dihydrophytol	157–159/0.8 mm.	73	(104)
3-Hydroxymethyl-2,6,10-trimethylhendeca-1,5,9-triene	95.5–96.5/0.01 mm.	80	(35)
2-Acetyl-5,9-dimethyldeca-4,8-dien-1-ol	104–106/0.01 mm.	99–100	(35)
	122/0.15 mm.		(181)
3-Hydroxymethyl-2,6,10-trimethylhendeca-5,9-dien-2-ol	127–130/0.01 mm.	161–162[g]	(35)
	175–178/0.45 mm.	165	(199)
An alcohol isomeric with the above[h]		182	(199)
2-Methyl-3-(4'-isopropylcyclohexyl)propan-1-ol	116–117/1.7 mm.	120.5–121	(151)
3,7-Dimethyl-1,7-octanediol	124–125/1 mm.	113 (mono-allophanate)[i]	(158)
		196–197 (diallophanate)	
3(4?)-Bromo-3-hexen-1-ol	68–69/3 mm.	171	(203)
Cyclocitronellol	84/4 mm.	172	(5)
		132 (stereoisomer)	(5)
cis-Cryptol	86/6 mm.	166–168	(72)
l-α-Terpineol	78–81/2.6 mm.	133–134	(152)
trans-Cryptol	90/4 mm.	196–197 (dec.)	(72)
2-Methyl-3-(4'-isopropylphenyl)propen-1-ol	130–130.5/4 mm.	171–172	(151)
3-Methyl-1-heptyn-3-ol	63/12 mm.	126–127	(127)
3-Hexyn-1-ol	66–67/13 mm.	187	(203)
2-Iodoethanol	85/25 mm.	182	(219)
1-Ethynylcyclohexanol	73–75/15 mm.	197	(138)
3-Propyl-1-hexyn-3-ol	69–71/12 mm.	143	(135)
3-Propyl-1-hexanol	78–79/16 mm.	133–134	(137)
4-Hepten-1-ol	81.5/17 mm.	168.8	(168)
4-Hepten-1-ol	81.5/17 mm.	168.5	(167)
Ethyl 2-hydroxy-3-methyl-3-butenoate	71–76/12 mm.	121	(215)
3-Propyl-1-hexen-3-ol	75–76/12 mm.	112	(136)

TABLE 1—*Continued*

ALCOHOL	BOILING POINT	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	°C.	
2,2,3-Trimethyl-6-hepten-3-ol	74/10 mm.	112	(37)
3-Methyl-1-octyn-3-ol	75/10 mm.	120	(127)
3,3-Dimethyl-1-ethynylcyclohexanol	81/11 mm.	157	(214)
2-Ethyl-2-hydroxymethyldioxolane	82/11 mm.	147	(229)
3,4,4-Trimethyl-2-penten-1-ol	84/12 mm.	77	(137)
2-(2'-Methyl-2'-dioxolanyl)ethanol	86/11 mm.	149	(229)
2,7-Dimethyl-1-octen-3-ol	85–87/11 mm.	87–88	(185)
d-2-Octanol	87/17 mm.	182–182.5	(148)
4-Octen-1-ol	95/17 mm.	160	(167, 168)
5-Methoxy-4-penten-1-ol	95.5/16 mm.	151	(170)
l-Tetrahydrolinaloöl	86–88/12 mm.	88	(6)
1-Hydroxymethyl-3-methylcyclohexene	88/11 mm.	172–173	(240)
1-Hydroxymethyl-3, 3-dimethylcyclohexene	88–92/11 mm.	163–164	(240)
2-Isopropenyl-2,3-dimethyl-4-penten-1-ol	89/12 mm.	179–180	(25)
2-Isopropyl-3,3-dimethyl-1-pentanol	89/11 mm.	163	(25)
4,7-Octadien-1-ol	90/12 mm.	153	(169)
3,7-Dimethyl-3-octanol	92–93/12 mm.	110–111	(6, 135)
(*d,l*-Tetrahydrolinaloöl)		108–109	(120)
5-Ethoxy-4-penten-1-ol	110/26 mm.	145	(170)
1-Cyclohexyl-2-propen-1-ol	93–94/13 mm.	169–170	(48)
2-Isopropenyl-4-methyl-4-hexen-1-ol	93/12 mm.	123	(126)
2-Isopropyl-4-methyl-1-hexanol	97–98/14 mm.	125	(126)
4-Bromo-4-penten-1-ol	97/15 mm.	138–139	(160)
Cycloöctanol	99/16 mm.	183.5	(173)
2-Methylene-4,4-dimethyl-1-hydroxymethylcyclohexane	99–100/15 mm.	163–164	(197)
d,l-γ,δ-Dihydrolavandulol	94/12 mm.	121	(183)
(5-Methyl-2-isopropenyl-1-hexanol)			
5-Methyl-2-isopropyl-3-hexen-1-ol	92–95/12 mm.	143–144	(191)
d,l-β,γ-Dihydrolavandulol	95/12 mm.	121–122	(191)
(5-Methyl-2-isopropyl-4-hexen-1-ol)			
Isolavandulol	95/11 mm.	120	(184)
d,l-Lavandulol	100–101/16 mm.	114–115	(26)
		119	(183)
		119–120	(184)
d,l-Tetrahydrolavandulol	96–97/12 mm.	99–100	(183, 191)
		100–101	(184)
1-Hydroxymethyl-2,2,4-trimethylcyclohexane	95–96/10 mm.	166–167	(196)
4-Nonen-1-ol	111–113/22 mm.	149.5	(161)
2-Hydroxyethyl butyrate	98–100/14 mm.	142	(83)
	106–108/16 mm.	117	(213)
trans-2-Isopropyl-5-methyl-3,5-hexadien-1-ol	94–97/11 mm. (lower-boiling fraction)	114–116	(191)

TABLE 1—*Continued*

ALCOHOL	BOILING POINT	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	°C.	
cis-2-Isopropyl-5-methyl-3,5-hexadien-1-ol	94–97/11 mm. (higher-boiling fraction)	78–80	(191)
2,3,6-Trimethylocta-6-en-1-yn-3-ol	96–97/11 mm.	138	(182)
3,5,5-Trimethylhepta-2,6-dien-1-ol	98–101/12 mm.	137–138	(26)
3-Propyl-2-hexen-1-ol	99–101/12 mm.	147–148	(137)
(+)-Cyclolavandulol	96–99/11 mm.	157–158	(24)
2,6-Nonadien-1-ol	95.5–100/11 mm.	140	(201, 202)
		145, 148	(174)
d,l-Cyclolavandulol	98–100/11 mm.	160	(24)
		163–164	(24)
2-(3',3'-Dimethylcyclohexylidene)ethanol	102–103/13 mm.	158–159	(214)
1,5,5-Trimethyl-4-hydroxymethylcyclohexene	110/15 mm.	157–158	(196)
2,7-Dimethyl-2-octen-1-ol	103–104/11 mm.	124–125	(185)
5,5-Dimethyl-1-cyclohexeneëthanol	102–103/12 mm.	183–184	(214)
2,7-Dimethyl-2,6-octadien-1-ol	106–108/12 mm.	122–123	(185)
1,3,3-Trimethyl-4-hydroxymethylcyclohexene	105–106/11 mm.	146–147	(196)
Citronellol	107–108/12 mm.	108–108.5	(150)
		112–113	(80)
3-(2'-Methyl-2'-dioxolanyl)-1-propanol	108/11 mm.	119	(229)
Tetrahydrogeraniol	98–100/7 mm.	117	(137)
		117–118	(25, 120)
4-Nonen-1-ol	118–119/23 mm.	149.5	(168)
2-Phenylpropan-1-ol	116/18 mm.	175	(141, 142)
d,l-β-Citronellol	118–119/18 mm.	104.5–105.5	(56)
Cyclononanol	112–113/13 mm.	177	(173)
4-Butyl-3-oxo-1-butanol	112–113/13 mm.	135	(229)
7-Hydroxycineole	108–111/9 mm.	169	(46)
l-Citronellol	108–109/10 mm.	106–107	(57)
d-Citronellol		105–106	(57)
2-(4'-Methylphenyl)propan-1-ol	124/17 mm.	157	(141, 142)
5-Butoxy-4-penten-1-ol	124–127/17 mm.	144	(170)
Myrcenol	123–128/17 mm.	110–111	(47)
Lactic acid	122/14 mm.	190	(207)
Cuminyl alcohol	122.5/13 mm.	201	(142)
2-Acyl-5-methyl-4-hexen-1-ol	122–123/11 mm.	146	(183)
2-(2',4'-Dimethylphenyl)ethanol	125/10 mm.	222	(85)
2-Acetyl-4-methyl-4-hexen-1-ol	123–124/13 mm.	151	(126)
α-Ionol	126.6–127/14.5 mm.	137–138[j]	(175)
β-Ionol	130.5/14.5 mm.	144–145	(175)
2-Butyl-1-octanol	132/15 mm.	119	(142)
2-Ethyl-3-phenyl-2-propen-1-ol	134/15 mm.	147	(141, 142)
Tetrahydroionol	134.5/15 mm.	164	(156)
2-Ethyl-3-phenyl-1-propanol	134–135/15 mm.	135	(142)

TABLE 1—*Continued*

ALCOHOL	BOILING POINT	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	°C.	
2-Methyl-2-undecanol	134–135/15 mm.	113.5	(11)
2-Benzyloxyethanol	137–138/17 mm.	156	(82, 155)
2-(2',2',3'-Trimethyl-1-cycloheptylidene)-ethanol	131–132/10 mm.	170	(178)
2-(2',2',3'-Trimethyl-1-cycloheptyl)ethanol	131–132/10 mm.	168	(178)
2-*o*-Anisylethanol	136/12 mm.	176–177	(84)
2-Methyl-2-(1'-hydroxy-6'-methyl-5-hepten-2'-yl)-1,3-dioxolane	136/11 mm.	102–103	(183)
2-Phenethyloxyethanol	140–142/15 mm.	150	(82, 155)
Irol	136–140/13 mm.	197	(175)
2-Hydroxyethyl pelargonate	143–144/14 mm.	142	(83)
1-Benzyloxy-2-butanol	151–152/18 mm.	102	(155)
3-Benzyloxy-1-propanol	155–157/20 mm.	119	(155)
2-(3'-Phenylpropoxy)ethanol	154–155/18 mm.	131	(82)
		131.5	(81, 155)
2-Butyl-3-phenyl-2-propen-1-ol	155/15 mm.	155	(141, 142)
2-Butyl-3-phenyl-1-propanol	155/15 mm.	144	(142)
3-(3'-Phenylpropoxy)-1-propanol	160/20 mm.	113	(155)
2-Amyl-2-nonen-1-ol	154/13 mm.	111.5	(142, 157)
2-Amyl-1-nonanol	154/13 mm.	120	(142, 157)
5-Phenyl-4-penten-1-ol	157/16 mm.	170.5	(167, 168)
2-Amyl-3-cyclohexyl-1-propanol	158/15 mm.	108	(142)
2-Amyl-3-phenyl-1-propanol	162/13 mm.	125	(142, 157)
2-Amyl-3-phenyl-2-propen-1-ol	162/12 mm.	160	(141, 142)
2-Hydroxyethyl phenylacetate	165–166/15 mm.	157–158	(83)
α-Santalol	166–167/14 mm.	162–163	(28)
4-(3'-Phenylpropoxy)-2-butanol	175/19 mm.	165	(155)
Lanceol	175–176/17 mm.	114–115	(27)
Santalol	170–178/17 mm.	162[k]	(210)
β-Santalol	177–178/17 mm.	159–160	(28)
2-Hexyl-3-phenyl-1-propanol	175–176/15 mm.	124	(142)
2-Hexyl-3-phenyl-2-propen-1-ol	176/15 mm.	142	(141, 142)
2-Hexyl-1-decanol	177/15 mm.	90	(142)
2-Heptyl-3-phenyl-2-propen-1-ol	186/15 mm.	139	(142)
2-Heptyl-3-phenyl-1-propanol	187/15 mm.	128	(142)
1,3-Diphenyl-1-propanol	194/15 mm.	99	(142)
2-Heptyl-1-undecanol	198/15 mm.	80	(142)
2-Octyl-3-phenyl-2-propen-1-ol	198/15 mm.	138	(141, 142)
2,3-Diphenyl-1-propanol	190–210/15 mm.	162	(142)
2-Octyl-3-phenyl-1-propanol	200–201/15 mm.	117	(142)
2,2-Dibenzylethanol	202/15 mm.	140	(142)
1,3-Diphenyl-1-butanol	202/15 mm.	148	(142)
1-(4'-Methylphenyl)-3-phenyl-1-propanol	200–202/13 mm.	111	(142)
2-Nonyl-3-phenyl-1-propanol	207–208/15 mm.	97	(142)
2-(8'-Nonen-1'-yl)-3-phenyl-2-propen-1-ol	212/17 mm.	127	(141, 142)
2-Nonyl-3-phenyl-2-propen-1-ol	212/17 mm.	132	(141)
		136	(142)

TABLE 1—*Concluded*

ALCOHOL	BOILING POINT	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	°C.	
2-(8′-Nonen-1′-yl)-3-phenyl-1-propanol	211/15 mm.	109	(142)
2-Octyl-1-dodecanol	215/15 mm.	69	(142)
2-Decyl-3-phenyl-2-propen-1-ol	221/15 mm.	137	(141, 142)
2-Decyl-3-phenyl-1-propanol	221–222/15 mm.	109	(142)
2-Benzyl-5-phenyl-1-pentanol	224/15 mm.	110	(142)
2-(8′-Nonen-1′-yl)-12-tridecen-1-ol	235/15 mm.	75	(142)
2-Nonyl-1-tridecanol	235/15 mm.	80	(142)
2-Decyl-1-tetradecanol	250/15 mm.	72	(142)
1-Phenyl-2,2-dibenzyl-1-ethanol	254–255/15 mm.	140	(142)

[a] Checked by reference 92.

[b] Checked by reference 125.

[c] *Analysis:* Calculated for $C_8H_{16}N_2O_3$: C, 51.04; H, 8.57; N, 14.89. Found: C, 50.65; H, 8.70; N, 15.1.

[d] The structure of this alcohol is in doubt, since it was made by treating a cyclohexene oxide with a Grignard reagent, a procedure which may lead to ring contraction. See reference 71 for a typical example.

[e] *Analysis:* Calculated for $C_7H_{12}N_2O_4$: C, 44.67; H, 6.43; N, 14.89. Found: C, 44.92; H, 6.13; N, 14.9.

[f] Karrer (116) reported "triticol" as $C_{19}H_{38}O$ or $C_{20}H_{40}O$ (phytol) and probably the latter.

[g] A diallophanate.

[h] See reference 198 for probable structure.

[i] In the monoallophanate one of the hydroxyl groups—probably the tertiary one—has been replaced by chlorine.

[j] J. Kandel (Compt. rend. **205,** 994 (1937)) reports the melting point as 151–152°C.

[k] Probably a mixture of the allophanates of α- and β-santalols.

TABLE 2

Allophanates of alcohols which are solid at 25°C.

ALCOHOL	MELTING POINT	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	°C.	
Anisyl alcohol	25	180.25	(11)
1-Methylcyclopentanol	36	157	(32)
2-Hydroxyethyl benzoate	36–37	179–180	(83)
2-Phenyl-2-propanol	37	124–126 (dec.)	(194)
Myristyl alcohol	38	156.0–156.5[a]	(21)
Menthol	43	133[b], 177[b]	(9, 10)
		213	(11)
		215	(145)
Cetyl alcohol	49	70	(70)
		153	(95)
1,1,1-Trifluoro-2-propanol	52	159.7 (dec.)	(200)
Piperonyl alcohol	52–53	176.5 (dec.)	(11)
1-Octadecanol	58.5	154.3–155.5	(237)
1-Phenyl-1,2-ethanediol	67	168 (monoallophanate)[c]	(154)
		240–241 (diallophanate)	(154)
Benzhydrol	69	181–182 (dec.)	(194)
Glycolic acid	79	192	(207)
1,5-Bis-(4'-methoxyphenyl)-3-pentanol	80–81	136 (block)	(50)
		137 (capillary)	(50)
l-4-(2',3',6'-Trimethylphenyl)-2-butanol	88.5–90.5	173–175	(162, 163)
1,1,1-Trichloro-2-methyl-2-propanol (Chlorobutanol)	97	114	(234)
Coprosterol	103–104	210–211	(205)
1,2-Diphenyl-1,2-ethanediol	134	280 (diallophanate)	(154)
Sitosterol	137	246–247 (charring)	(205)
Dihydrocholesterol (Cholestanol)	141.5–142	255–256[d]	(205)
Dihydrocryptosterol (Dihydrolanosterol)	145–146	249 (dec.)	(172)
Cholesterol	148.5	214–215[e]	(102)
		235–236[d, f]	(205)
		277–278	(63)
Testosterone	153.5–154.5	229.8–230.3[g]	(92)
Ergosterol	163	250[h]	(233)
Stigmasterol	169–170	241–242[i]	(102)
Pregnenolone	183–186	239.8–240.3 (dec.)[j]	(125)

[a] *Analysis:* Calculated for $C_{16}H_{32}N_2O_3$: C, 63.96; H, 10.74; N, 9.33. Found: C, 64.00, 63.66; H, 10.59, 10.51; N, 9.49.

[b] The structure of this alcohol is in doubt, since it was made by treating a cyclohexene oxide with a Grignard reagent, a procedure which may lead to ring contraction. See reference 71 for a typical example.

[c] The position of the ester was not specified.

[d] Checked by reference 125.

[e] This is cholesteryl carbamate, which was obtained by Kaighin, using four-times-recrystallized cyanuric acid as the source of cyanic acid. *Analysis:* Calculated for $C_{28}H_{47}NO_2$: C, 78.27; H, 11.02; N, 3.26. Found: C, 78.10; H, 11.12; N, 3.28.

[f] Checked by reference 92.

[g] *Analysis:* Calculated for $C_{21}H_{30}N_2O_4$: C, 67.34; H, 8.09; N, 7.48. Found: C, 67.65; H, 7.90; N, 7.37.

[h] Checked by reference 102.

[i] *Analysis:* Calculated for $C_{31}H_{50}N_2O_3$: C, 74.65; H, 10.11; N, 5.62. Found: C, 74.62; H, 10.08; N, 6.09.

[j] *Analysis:* Calculated for $C_{23}H_{34}N_2O_4$: C, 68.63; H, 8.51; N, 6.96. Found: C, 68.12; H, 8.38; N, 7.04.

TABLE 3

Allophanates of alcohols for which no physical constants are given

ALCOHOL	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	
Ricinolein	61–62	(211)
6-Nonen-3-ol	96	(202)
l-Tetrahydrolavandulol	101–102	(183)
2-(*p-tert*-Butylphenoxy)ethanol	117–121	(237)
3-Methyl-2-oxo-3-pentanol	120.5	(189)
1,6-Nonadien-3-ol	125	(202)
Amyl lactate	131	(207)
9-Octadecen-1-ol	135	(3)
Undecelenyl alcohol	143	(11)
5-Methyl-1-hexen-3-ol	147.5	(46)
Cyclohexylbutanol	148	(11)
1,2,2,2-Tetrachloroethanol	160	(212)
2,4,4-Trimethyl-1-hydroxymethylcyclohexane	163–164	(197)
d,l-Dihydrocyclolavandulol	163–164	(24)
2-Methyl-2-hepten-4-ol	171	(79)
Ethylvanillyl alcohol	173	(11)
Methyl saligenin	180	(11)
tert-Menthol	187	(11)
"Oxycamphor"	204	(145)
Isopulegyl alcohol	219	(11)
β-Amyrin	250	(62)
	273–275	(13, 206)

TABLE 4

Allophanates of phenols

PHENOL	BOILING POINT	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	°C.	
2-Chlorophenol	175–176	179	(78)
Phenol	181	150 (dec.)	(208)
		180	(11)
		194	(23)
o-Cresol	191	185	(11)
p-Cresol	202	194	(11)
Methyl salicylate	223	175	(145)
Monomethoxytocol	180–190/0.03 mm.	105–107	(105)
	MELTING POINT		
2-Methoxyphenol	28	176	(145)
		200	(23)
2-Ethoxyphenol	28	212	(23)
2,2-Didodecyl-5,7,8-trimethyl-6-hydroxychroman	28	116	(97)
o-Cresol	30	185	(11)
p-Cresol	35–36	194	(11)
Phenol	42–43	180	(11)
		194	(23)
Thymol	51.5	190	(70)
2-Dodecyl-2,5,7,8-tetramethyl-6-hydroxychroman	60–61	180	(97)
2,3,5,6-Tetramethyl-4-chaulmoogryloxyphenol	61	174	(221)
2,3,6(2,3,5?)-Trimethyl-4-dodecyloxyphenol	81	184	(220)
2,2,5,7,8-Pentamethyl-6-hydroxychroman	93–94	230	(97)
2,3,5,6-Tetramethyl-4-dihydrophytyloxyphenol	97	178–180	(117)
		182–183	(65, 221)
Resorcinol	111	120	(207)
2-Ethyl-4,6,7-trimethyl-5-hydroxychroman	120	214	(106)
2,5,7,8-Tetramethyl-6-hydroxychroman	145	220	(97)
1,7-Dihydroxynaphthalene	178	243 (diallophanate)	(128)

TABLE 5

Allophanates of phenols for which no physical constants are given

PHENOL	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	
Methylmethoxytocol	103 (not sharp)	(105)
d,l-5,7-Diethyltocol	107	(118)
2,2-Dicetyl-5,7,8-trimethyl-6-hydroxychroman	109	(96)
2,3,6-Trimethyl-4-[3'-methyl-5'-(2",2",6"-trimethylcyclohex-1"-yl)amyl-1'-oxy]phenol	128	(222)
γ-Tocopherol	135	(116)
	136–138	(8)
	137–140	(59)
2-Tridecyl-5,7-dimethyl-6-hydroxychroman (Isophytol)	143	(111)
7,8-Dimethyltocol	146	(110)
β-Tocopherol	137	(116)
	138–139	(8)
	143–144	(109, 110, 116)
	143.5–144.5	(206)
	147	(94)
2-Propyl-2-(4',8',12'-trimethyltridecyl)-5,7,8-trimethyl-6-hydroxychroman	146–148	(119)
2-Methyl-2-(4',8',12'-trimethyltridecyl)-7,8-trimethylene-6-hydroxychroman	149	(113)
2-Ethyl-2-(4',8',12'-trimethyltridecyl)-5,7,8-trimethyl-6-hydroxychroman	150–152	(119)
5,8-Dimethyltocol	154	(110)
d,l-5,7-Dimethyltocol	150	(107)
(β-Tocopherol?)	154–155	(107)
5,7-Dimethyl-8-methoxytocol	159–161	(105)
2,5,7,8-Tetramethyl-2-(4',8',12',16'-tetramethylheptadecyl)-6-hydroxychroman	161	(88)
2-Methyl-2-(4',8',12'-trimethyltridecyl)-7,8-tetramethylene-6-hydroxychroman	162–163	(113)
d,l-3,4-Dehydro-α-tocopherol	163	(89, 114)
d,l-5,8-Diethyl-7-methyltocol or *d,l*-7,8-Diethyl-5-methyltocol	165	(108)
2,5,7,8-Tetramethyl-2-(4',8'-dimethylnonyl)-6-hydroxychroman	170	(87)
2,5,7-Trimethyl-8-ethyl-2-(4',8',12'-trimethyltridecyl)-6-hydroxychroman	170–171	(103)
2,3,5,6-Tetramethyl-4-[3'-methyl-5'-(2",2",6"-trimethylcyclohex-1"-yl)-amyl-1'-oxy]phenol	173–174	(222)
2,3,5,6-Tetramethyl-4-phytyloxyphenol	176	(117)
α-Tocopherol	157–158	(8)
	158–159	(13)
	158–160	(62, 206)
	170–172	(98)
	172	(109, 114, 115)
	175–176 (*d,l*)	(99)
Iso-α-tocopherol	174–175	(95)
	176	(96, 100)

TABLE 5—*Concluded*

PHENOL	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	
2-(6′,10′,14′-Trimethyl-2′-pentadecyl)-4,6,7-trimethyl-5-hydroxycoumaran	176–180	(192)
5,7,8-Trimethyl-2,2-pentamethylene-6-hydroxychroman	184–186	(112)
2,3,5,6-Tetramethyl-4-(4′-methyl-2-pentyloxy)-phenol	206	(222)
2,3,5,6-Tetramethyl-4-dodecyloxyphenol	223	(221)
2,4,6,7-Tetramethyl-5-hydroxycoumaran	230	(222)
2,4,6,7-Tetramethyl-5-hydroxychroman	230	(222)

TABLE 6

Allophanates of miscellaneous alcohols

ALCOHOL	MELTING POINT OF ALLOPHANATE	REFERENCES
	°C.	
$NH_2COOCH(CH_3)S_2CH(CH_3)OCONHCONH_2$	192–193	(216)
$NH_2COCH(CH_3)S_2CH(CH_3)OCONHCONH_2$	213	(216)
β-Hydroxyethyltrimethylammonium iodide	254–255 (dec.)	(219)

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