table by digitonin and containing one or two hydroxyl groups are either unsaturated sterols or belong to the *allo*-saturated series, with none of the regular pregnane series present.

Summary

Cholesterol and *allo*-pregnanediol-3(β),20(α) were isolated from the digitonin precipitable fraction of human pregnancy urine sterols. No mono- or dihydroxy-steroids of the pregnane configuration at C-5 with 3(β)-OH groups were found present.

STATE COLLEGE, PENNA. RECEIVED JUNE 15, 1938

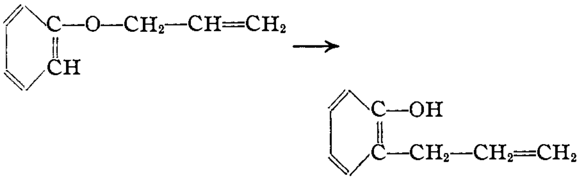
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Rearrangement of Vinyl Allyl Ethers

BY CHARLES D. HURD AND MAXWELL A. POLLACK

That phenyl allyl ether undergoes thermal rearrangement into *o*-allylphenol has been known for several years. Recent investigations have demonstrated the intramolecular nature of the process,[1] the inversion of the allyl group,[2] the failure of α,α-disubstituted allyl ethers to rearrange,[3] and the unusual rearrangement of γ-ethylallyl phenyl ether.[4]

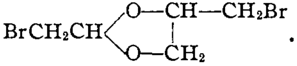
That part of the aryl allyl ethers which is concerned in the rearrangement possesses the skeleton C=C—O—C—C=C



There is no previous mention in the literature of vinyl allyl ether, the simplest compound to possess this structure. It seemed important, therefore, to prepare it so that its pyrolytic behavior might be studied. If a comparable rearrangement occurred, allylacetaldehyde would be anticipated.

$$\begin{array}{l} \mathrm{CH{-}O{-}CH_2CH{=}CH_2} \\ \| \\ \mathrm{CH_2} \end{array} \longrightarrow \begin{array}{l} \mathrm{CH{=}O} \\ | \\ \mathrm{CH_2{-}CH_2{-}CH{=}CH_2} \end{array}$$

The enol modification of this aldehyde, $CH_2{=}CH{-}CH_2{-}CH{=}CHOH$, would be analogous to the *o*-allylphenol.

Since neither vinyl allyl ether nor any of its simple analogs are known, several synthetical approaches were tested. One of these methods consisted in the condensation between allyl bromoacetal and sodium. A similar reaction had been employed successfully by Wislicenus[5] in the preparation of vinyl ethyl ether: $BrCH_2CH(OC_2H_5)_2 + Na \longrightarrow CH_2{=}CHOC_2H_5 + NaBr + C_2H_5ONa$, but in the present adaptation, the yield was trivial. When only one-fifth of the theoretical amount of sodium was added to the acetal, the reaction mixture became a thick brown mass, to which further addition of alkali metal proved ineffectual. No improvement was realized with xylene as solvent. Somewhat similar results were obtained by Hibbert and Hill[6] from the reaction between sodium and 3-bromo-1,2-propanediol bromoacetal, .

Another procedure tried was related to the last step in Boord's[7] synthesis of α-olefins from β-bromo ethers: $BrCH_2CHROC_2H_5 + Zn \longrightarrow CH_2{=}CHR + BrZnOC_2H_5$. Here again, however, the analogy was misleading for only slight yields of vinyl allyl ether were obtained following the action of zinc on allyl bromoacetal, $BrCH_2CH(OC_3H_5)_2$. With no solvent, very little reaction occurred below 148°, and above that temperature the violence of reaction led to the formation of a black tar. When boiling alcohol was used as a medium, it was found that the rate of reaction was very slow, only a small amount of ether being obtained in six hours.

Another approach to the synthesis of this material was based on the fact that enol ethers may be prepared by heating certain ketals in the presence of an acid catalyst.[8] When allyl acetal was heated with a trace of *p*-toluenesulfonic acid, a small amount of vinyl allyl ether was obtained, but most of the material remained unreacted.

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(1) Hurd and Schmerling, THIS JOURNAL, **59**, 107 (1937).

(2) Claisen and Tietze, *Ber.*, **58**, 275 (1925).

(3) Claisen and co-workers, *J. prakt. chem.*, **105**, 67 (1922); Hurd and Cohen, THIS JOURNAL, **53**, 1919 (1931).

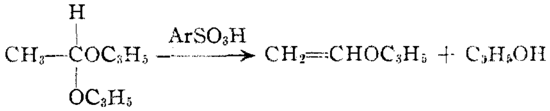
(4) Lauer and Filbert, *ibid.*, **58**, 1388 (1936).

(5) Wislicenus, *Ann.*, **192**, 106–112 (1879).

(6) Hibbert and Hill, THIS JOURNAL, **45**, 746 (1923).

(7) Dykstra, Lewis and Boord, *ibid.*, **52**, 3401 (1930).

(8) Johannissian and Akunian, *Bull. univ. etat R. S. S.-Armenie* No. **5**, 245–249 (1930); *C. A.* **25**, 921 (1931); Killian, Hennion and Nieuwland, THIS JOURNAL, **57**, 544 (1935).



$$CH_3{-}\underset{\displaystyle OC_3H_5}{\overset{\displaystyle H}{C}}OC_3H_5 \xrightarrow{ArSO_3H} CH_2{=}CHOC_3H_5 + C_3H_5OH$$

Killian, Hennion and Nieuwland were unable to obtain vinyl ethers by similar treatment of ethyl and propyl acetals.

One method which was found to be fairly serviceable involved heating allyl acetal with phosphorus pentoxide in a solvent such as quinoline or dimethylaniline.

$$CH_3CH(OC_3H_5)_2 + P_2O_5 \longrightarrow CH_2{=}CH{-}O{-}C_3H_5 + 2HPO_3$$

Yields of 12–19% were obtained. Claisen[9] used this general method in 1898 in preparing vinyl ethyl ether.

The best synthesis of vinyl allyl ether was found to be the reaction between β-bromoethyl allyl ether and powdered potassium hydroxide. A 51% yield was realized.

$$BrCH_2CH_2OCH_2CH{=}CH_2 + KOH \longrightarrow CH_2{=}CHOCH_2CH{=}CH_2 + KBr + H_2O$$

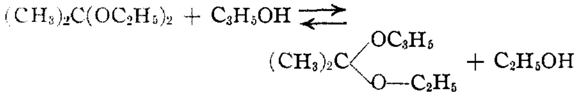
Bromoethyl allyl ether was prepared for this purpose by condensing the sodium salt of ethylene glycol with allyl bromide (77–81% yields), and treating the resulting β-hydroxyethyl allyl ether in pyridine with phosphorus tribromide.

$$HOCH_2CH_2ONa + BrCH_2CH{=}CH_2 \longrightarrow HOCH_2CH_2OCH_2CH{=}CH_2 \xrightarrow{PBr_3} BrCH_2CH_2OCH_2CH{=}CH_2.$$

Yields of 35–45% were obtained in this last reaction. There was considerable splitting of the ether during this treatment, which accounted for the low yield.

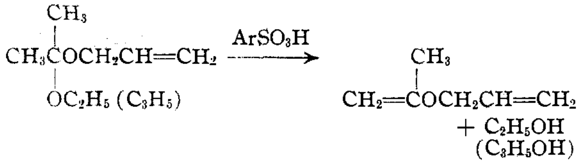
It will be recalled that the attempts to prepare vinyl allyl ether from allyl acetal were unsuccessful. A similar reaction with allyl dimethylketal, however, yielded acceptable quantities of α-methylvinyl allyl ether. For this synthesis, ethyl dimethylketal, $(CH_3)_2C(OC_2H_5)_2$, was required. It was obtained readily when acetone was condensed with ethyl orthoformate and ethyl alcohol in the presence of p-toluenesulfonic acid. When this ketal was heated for a few minutes with an excess of allyl alcohol and the same catalyst, an interchange of groups occurred and allyl dimethylketal was isolable from the reaction mixture in 38% yield. A smaller amount (12%) of the mixed ketal was also obtained.

$$(CH_3)_2C(OC_2H_5)_2 + 2C_3H_5OH \overset{ArSO_3H}{\rightleftarrows} (CH_3)_2C(OC_3H_5)_2 + 2C_2H_5OH$$



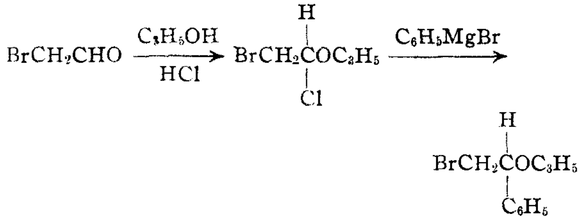
$$(CH_3)_2C(OC_2H_5)_2 + C_3H_5OH \rightleftarrows (CH_3)_2C\begin{cases}OC_3H_5\\O{-}C_2H_5\end{cases} + C_2H_5OH$$

When either of these allyl dimethylketals was distilled slowly from p-toluenesulfonic acid, α-methylvinyl allyl ether was obtained.



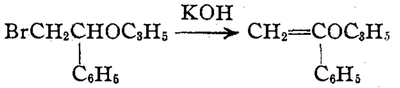
$$CH_3\underset{\displaystyle OC_2H_5\,(C_3H_5)}{\overset{\displaystyle CH_3}{C}}OCH_2CH{=}CH_2 \xrightarrow{ArSO_3H} CH_2{=}\overset{\displaystyle CH_3}{C}OCH_2CH{=}CH_2 + C_2H_5OH\ (C_3H_5OH)$$

The work of Boord and Lauer and their coworkers[10] on the preparation of vinyl ethers was adapted to this synthesis. α-Chloro-β-bromoethyl allyl ether, prepared by allowing dry hydrogen chloride and allyl alcohol to react with a mixture of bromoacetaldehyde and its trimer, was condensed with phenylmagnesium bromide. In this way, α-phenyl-β-bromoethyl allyl ether was formed.



$$BrCH_2CHO \xrightarrow[HCl]{C_3H_5OH} BrCH_2\underset{\displaystyle Cl}{\overset{\displaystyle H}{C}}OC_3H_5 \xrightarrow{C_6H_5MgBr} BrCH_2\underset{\displaystyle C_6H_5}{\overset{\displaystyle H}{C}}OC_3H_5$$

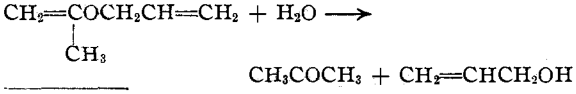
When it was heated with powdered potassium hydroxide, α-phenylvinyl allyl ether was produced.



$$BrCH_2\underset{\displaystyle C_6H_5}{C}HOC_3H_5 \xrightarrow{KOH} CH_2{=}\underset{\displaystyle C_6H_5}{C}OC_3H_5$$

Acid Hydrolysis of the Vinyl Ethers.—It is known[11] that allyl ethers hydrolyze readily when exposed to aqueous solution of acid. The three new vinyl ethers were also subjected to acid hydrolysis for purposes of characterization. Acetaldehyde, acetone and acetophenone were formed in turn.

$$CH_2{=}CHOCH_2CH{=}CH_2 + H_2O \xrightarrow{HCl} CH_3CHO + CH_2{=}CHCH_2OH$$



$$CH_2{=}\underset{\displaystyle CH_3}{C}OCH_2CH{=}CH_2 + H_2O \longrightarrow CH_3COCH_3 + CH_2{=}CHCH_2OH$$

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[9] Claisen, *Ber.*, **31**, 1021 (1898).

[10] Swallen and Boord, THIS JOURNAL, **52**, 651 (1930); Dykstra, Lewis and Boord, *ibid.*, **52**, 3396 (1930); Lauer and Spielman, *ibid.*, **53**, 1533 (1931).

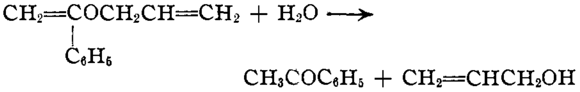
[11] Lauer and Spielman, *ibid.*, **53**, 1533 (1931).

TABLE I

PROPERTIES OF NEW COMPOUNDS

Compound	B. p., °C.	Press., mm.	n^{20}D	d^{20}_4	Mol. ref. Found	Mol. ref. Calcd.
Vinyl allyl ether	65.0–65.2	733	1.4115	0.805	25.98	26.00
α-Methylvinyl allyl ether	87.5–88.0	745	1.4191	0.808	30.67	30.62
α-Phenylvinyl allyl ether	104–105	12	1.5402	1.007	49.91	50.34
β-Hydroxyethyl allyl ether	63–64	18–19	1.4356	0.958	27.84	27.99
β-Bromoethyl allyl ether	68.5–69.0	36	1.4668	1.336	34.22	34.23
α-Phenyl-β-bromoethyl allyl ether	129–130	12	1.5421	1.299	58.40	58.61
Allyl acetal[a]	148–149	753	1.4242	0.877	41.41	41.50
Allyl dimethylketal	61	26	1.4254	.870	45.93	46.11
Ethyl allyl dimethylketal	43–45	26	1.4090	.852	41.85	41.96
Allyl bromoacetal	102–104	23	1.4729	1.269	48.86	49.38
Allylacetaldehyde	103–104	749	1.4191	0.852	24.92	24.83

[a] Nieuwland and co-workers, THIS JOURNAL, **45**, 1552 (1923), and **52**, 2892 (1930), obtained materials with the boiling points of 162° (atm.) and 90–93° (16 mm.), n^{28}D 1.4351, which he considered to be allyl acetal. However, in view of the discrepancies between these values and the ones found here, and the fact that no other constants or analyses were given by Nieuwland, it seems possible that the material obtained by him either was not the acetal or was a very impure sample.

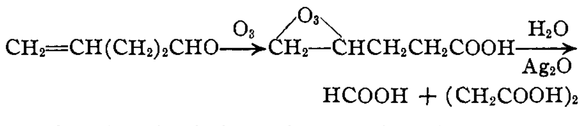


$$\underset{\displaystyle C_6H_5}{CH_2{=}COCH_2CH{=}CH_2} + H_2O \longrightarrow CH_3COC_6H_5 + CH_2{=}CHCH_2OH$$

Pyrolysis of the Ethers.—Heating in the liquid phase to 200–250° is the general method of bringing about the rearrangement of aryl allyl ethers into phenols. Whether or not vapor phase heating of vinyl allyl ether, necessitated by the low boiling point of the latter, would be comparable, could not be predicted. It was found, however, that the anticipated rearrangement into allylacetaldehyde occurred to the extent of 40–50% at 255°.

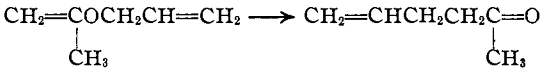
$$CH_2{=}CHOCH_2CH{=}CH_2 \longrightarrow CH_2{=}CHCH_2CH_2CHO$$

No other products were formed, the remainder of the material being unchanged ether. At 215°, no rearrangement was observable. The identity of allylacetaldehyde was confirmed by analyses and by treatment with ozone, which gave rise to formic and succinic acids.



$$CH_2{=}CH(CH_2)_2CHO \xrightarrow{O_3} \overset{\quad O_3 \quad}{CH_2{-}CH}CH_2CH_2COOH \xrightarrow[Ag_2O]{H_2O} HCOOH + (CH_2COOH)_2$$

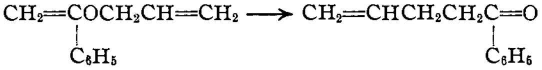
α-Methylvinyl allyl ether was found to be somewhat less stable to heat. There was practically complete conversion into allylacetone by heating in the vapor phase at 255°.



$$\underset{\displaystyle CH_3}{CH_2{=}COCH_2CH{=}CH_2} \longrightarrow \underset{\displaystyle CH_3}{CH_2{=}CHCH_2CH_2C{=}O}$$

Indeed, a small amount of this ketone was isolated during the preparation of the ether, in which process the bath temperature reached 200°.

α-Phenylvinyl allyl ether appeared to be the least stable of these ethers. Mere distillation under reduced pressure (temperature below 175°) caused rearrangement into ω-allylacetophenone, and brief refluxing under atmospheric pressure brought about this reaction in a high yield.



$$\underset{\displaystyle C_6H_5}{CH_2{=}COCH_2CH{=}CH_2} \longrightarrow \underset{\displaystyle C_6H_5}{CH_2{=}CHCH_2CH_2C{=}O}$$

Experimental Part

Bromoacetaldehyde.—Paraldehyde (125 g.) was brominated at −5 to −10° with bromine (360 g.) according to the directions of Hibbert and Hill.[12] The yields of the lachrymatory mixture of bromoacetaldehyde and its trimer were 39–53%.

Allyl Bromoacetal.—Seventy grams of the above bromoacetaldehyde mixture was placed in a 500-cc. three-necked flask, equipped with a mercury-sealed stirrer and a reflux condenser which was protected from moisture by a calcium chloride tube. To this were added 69 g. of allyl alcohol (b. p. 93–95°) and 0.4 cc. of 40% sulfuric acid. The resulting solution was refluxed, with constant stirring, for nine hours on the steam-bath. After cooling, it was taken up in an equal volume of ether and neutralized by shaking with a dilute sodium hydroxide solution. It was further washed with a small amount of sodium bisulfite solution, then washed with water, and dried over anhydrous sodium sulfate.

The ether solution was filtered and the ether removed under diminished pressure. The reddish-brown residual liquor was distilled under reduced pressure. Redistillation gave pure allyl bromoacetal, boiling at 102–104° at 23 mm. The material was colored slightly yellow when freshly distilled, but became colorless on standing. Constants for this compound, and for the other compounds to be described in this paper, are collected in Table I.

Anal. Calcd. for $C_8H_{13}O_2Br$: Br, 36.16. Found: Br, 35.94.

The yield obtained in this way was 20.5%. The yield

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[12] Hibbert and Hill, THIS JOURNAL, **45**, 746 (1923).

was increased to 26.4% by removal of the water formed in the reaction. An experiment using 91.5 g. of the aldehyde, 90 g. of dry allyl alcohol and 0.55 cc. of 40% sulfuric acid was carried out. During a similar heating period of nine hours, 24 cc. of an alcohol–water constant-boiling mixture was removed, while 40 cc. of the alcohol was added. On working up the products as before, 43.4 g. of the acetal was obtained. If the allyl alcohol (53% of calcd.) was added directly to the bromination product of paraldehyde as soon as the color of bromine had disappeared from the solution, the yield of the acetal was 25%. In this reaction, stirring at −5° was maintained for two and a half hours before allowing the flask to warm up to room temperature. The lower layer was separated, dissolved in ether and purified as before.

Effect of Metals on Allyl Bromoacetal

Sodium.—Small pieces of sodium were added to 9.6 g. of allyl bromoacetal at 140–145°. About four drops of water-insoluble, odoriferous liquid, $n^{20}D$ 1.4105, was collected as distillate, which was identified later as vinyl allyl ether. When only 0.4 g. of sodium was added the reaction mixture set to a brown mass from which half of the original bromoacetal was recoverable (b. p. 103–105° at 27 mm.). Additional sodium rested on the surface of the brown mass without reacting. Xylene, as diluent, did not prevent the formation of this brown sludge.

Zinc.—Little or no reaction occurred between allyl bromoacetal and zinc dust up to 148°, but at this temperature a violent exothermic reaction ensued. A black tar was the only product.

A mixture of 20 g. of allyl bromoacetal, 50 cc. of alcohol and 14.7 g. of zinc dust was heated to reflux temperatures and stirred for three hours. Then 20 cc. of distillate (A) was taken off and 20 cc. of alcohol added for another refluxing period of three hours, after which all that would distil over (B) on the steam-bath was collected. Both A and B smelled strongly of allyl vinyl ether. When A was mixed with an equal volume of water, about 0.5 cc. of it separated, $n^{20}D$ 1.4101. No separation occurred when B was diluted. Much allyl bromoacetal was recovered from the higher boiling residue.

Allyl Acetal.—Twenty grams of dry calcium chloride was dissolved in 132 g. of allyl alcohol (b. p. 93–96°) by shaking in a tightly stoppered bottle. This solution was cooled to 0° and 50 g. (1.14 moles) of cold acetaldehyde was added. The bottle was restoppered and the mixture was shaken vigorously for ten minutes, at the end of which time two layers had formed.

The mixture was allowed to stand for thirteen and one-half hours with occasional shaking, before separating the clear upper layer. This was washed with 100 cc. of distilled water in three portions. The washed oil was allowed to stand for three hours to permit more water to settle out, and was then dried over anhydrous potassium carbonate for eighteen hours. After filtering, the material was distilled. Refractionation gave a total of 110.5 g. (68.2% yield) of allyl acetal which boiled between 146–150°. Other runs gave yields of 62.4 and 64.7%. The pure material boiled at 148–149°.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.61; H, 9.88. Found: C, 67.14, 67.37; H, 9.88, 9.95.

Decomposition of Allyl Acetal in the Presence of *p*-Toluenesulfonic Acid.—A mixture of 16 g. of allyl acetal and 0.045 g. of *p*-toluenesulfonic acid was heated to refluxing on an oil-bath. A small amount of tar appeared and the solution became red-brown in color. Subsequently, the material was heated at 105° for two and one-half hours and then at 130–140° for ten hours. During this latter heating period, 3 g. of liquid distilled over. Redistillation of this distillate gave 1.82 g. of crude vinyl allyl ether, collected between 48–98°. The usual ethereal odor was observed with this material. Its index of refraction $n^{20}D$ was 1.4107 ($n^{20}D$ for the pure ether, 1.4115). Evidence for its structure was obtained by hydrolysis of a small portion with dilute hydrochloric acid. To this resulting solution was added 5 cc. of an alcoholic solution of 2,4-dinitrophenylhydrazine. The hydrazone melted (without recrystallization) at 151–152°; mixed melting point with an authentic sample of the acetaldehyde derivative (m. p. 161–163°) was 157–158°.

Reaction between Allyl Acetal and Phosphorus Pentoxide.—Sixty grams of dimethylaniline (b. p. 190–191°) and 60 g. of phosphorus pentoxide were mixed thoroughly in a 500-cc. flask, after which 59 g. of allyl acetal was added. A 25-cm. empty Hempel column was placed on top of the flask and was connected to a condenser set for distillation. The mixture was heated slowly and kept at gentle refluxing until all of the easily-volatile material had distilled over. During this period a considerable amount of tarring occurred. The total weight of distillate was 28.8 g. Fractionation of this material through a 25-cm. Widmer column gave 6.8 g. (19.3%) of crude vinyl allyl ether (b. p. 56–70°). The other fractions consisted mainly of allyl alcohol (app. 60% of total), some allyl acetal and 1 g. of an unidentified substance boiling at 40–42°.

Other runs gave essentially the same products. The yields of vinyl allyl ether obtained in these other cases were: 15.5% (crude, using dimethylaniline as solvent) and 11.5% (pure, using quinoline as solvent). One redistillation through a good column sufficed for the purification of the ether, b. p. 65.0–65.2°.

Anal. Calcd. for C_5H_8O: C, 71.38; H, 9.59. Found: C, 71.30; H, 9.39.

β-Hydroxyethyl Allyl Ether.—To 158 g. of redistilled ethylene glycol 23.4 g. of sodium was added slowly in small pieces. After the reaction was over, the solution was heated with stirring on the steam-bath while 124 g. of allyl bromide was slowly added. The mixture was heated for two hours after the addition. The sodium bromide was filtered off and the filtrate distilled under reduced pressure. Redistillation through a 60-cm. Vigreux column gave 79.6 g. of pure material boiling between 63–64° at 18–19 mm., yield 77%.

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.81; H, 9.87. Found: C, 58.45; H, 9.79.

Another run using 0.91 mole of sodium and 1.2 moles of allyl bromide wherein the ethylene glycol was separated from the β-hydroxyethyl allyl ether by ether–water partition, and the last of the hydroxy ether recovered by extracting the aqueous solution with ether, gave an 81% yield after the usual procedures of drying and distilling.

β-Bromoethyl Allyl Ether.—To 75.3 g. (0.278 mole) of phosphorus tribromide in a flask surrounded by an icebath was added slowly, with constant stirring, a mixture of 71 g. (0.695 mole) of β-hydroxyethyl allyl ether and 12.5 g. (0.156 mole) of dry pyridine. The mixture was stirred for one hour and then allowed to stand for an equal interval before distilling under reduced pressure. The distillate was washed twice with dilute sodium hydroxide, twice with dilute sulfuric acid, and once with water. After drying over anhydrous sodium sulfate, distilling and redistilling through a 60-cm. Vigreux column, a 40% yield of β-bromoethyl allyl ether was obtained. It boiled at 68.5–69° (36 mm.).

Anal. Calcd. for C_6H_9OBr: Br, 48.43. Found: Br, 48.19.

Using the Palomaa and Kenetti procedure,[13] which consists of the addition of the alcohol–pyridine mixture to cold phosphorus tribromide and allowing the reaction mixture to stand for a few hours, unmodified except that the crude bromide was distilled off under reduced pressure as soon as the addition was over, a 45% yield was obtained.

In another run, wherein the phosphorus tribromide was added to the mixture of β-hydroxyethyl allyl ether and pyridine at 0°, and the whole allowed to stand overnight, a 35% yield was realized.

Reaction between β-Bromoethyl Allyl Ether and Potassium Hydroxide.—Into a 125-cc. distilling flask was placed 42.5 g. of β-bromoethyl allyl ether, after which 43 g. of finely powdered potassium hydroxide was added. The mixture was heated slowly on an oil-bath to 110°, at which point volatile material began to distil. The bath temperature was raised slowly. When no more would come over (bath temperature was 174°), the heating was stopped. The distillate weighed 11.1 g. That this material was vinyl allyl ether was shown by the fact that practically all of it distilled at 65–66° (741 mm.). The refractive index, $n^{24}\text{D}$ 1.4101, was also in good agreement. The yield was 51%.

Upon taking up the residue in the flask with water, 12 cc. of impure bromoethyl allyl ether was recovered.

Ethyl Dimethylketal.—A mixture of 39 g. (0.26 mole) of ethyl orthoformate, 13 g. (0.23 mole) of dry acetone, 58 g. (1.3 moles) of absolute alcohol and 0.055 g. of *p*-toluenesulfonic acid was refluxed for ten minutes, neutralized with sodium ethoxide, cooled with running water and diluted with 400 cc. of distilled water. The upper layer which separated was washed three times with 50-cc. portions of distilled water and then allowed to dry over anhydrous potassium carbonate. After filtering, the material was distilled and the portion boiling between 113–115° was collected. The yield was 22.6 g. (75%).

Allyl Dimethylketal and Ethyl Allyl Dimethylketal.—To a mixture of 54 g. (0.41 mole) of ethyl dimethylketal and 160 g. of dry allyl alcohol was added 0.1 g. of *p*-toluenesulfonic acid. The whole was refluxed for ten minutes and then the color was discharged with sodium ethoxide. The alcohol mixture was distilled off slowly (up to a temperature of 97°), using a 60-cm. electrically heated Vigreux column with partial condensation head. The remainder was fractionated through this same column under reduced pressure. Refractionation gave 7 g. (12%) of ethyl allyl dimethylketal boiling at 43–45° at 26 mm., and 24 g. (38%) of allyl dimethylketal, boiling at 61° at 26 mm. (also 46–48° at 13–14 mm.).

Anal. of ethyl allyl dimethylketal. Calcd. for $C_8H_{16}O_2$: C, 66.62; H, 11.19. Found: C, 67.00; H, 11.23.

Anal. of allyl dimethylketal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.31. Found: C, 69.18; H, 10.35.

α-Methylvinyl Allyl Ether.—To 25 g. of allyl dimethylketal was added 0.1 g. of *p*-toluenesulfonic acid in a 50-cc. flask topped with a short Vigreux column connected to a water condenser set for distillation. The material was heated to gentle refluxing on an oil-bath, whereupon 21 g. of a volatile distillate was collected during a period of five hours. The bath temperature changed from 145 to 200° during this time. The distillate was shaken with four times its volume of distilled water, and the separated upper layer washed twice more with equal volumes of distilled water, after which the weight was 12 g. After drying over anhydrous potassium carbonate, the material was filtered and distilled through a 60-cm. Vigreux column. Three and one-half grams of α-methylvinyl allyl ether was collected, boiling at 87.5–88° (745 mm.). A small amount (1.5 g.) of allylacetone was separated at 126–129°. The residue was mainly unreacted allyl dimethylketal.

The allylacetone was characterized by its semicarbazone, m. p. 102–103° (reported[14] as 100–102°). The ether was analyzed.

Anal. Calcd. for $C_6H_{10}O$: C, 73.41; H, 10.28. Found: C, 73.02; H, 10.03.

Decomposition of Ethyl Allyl Dimethylketal in the Presence of *p*-Toluenesulfonic Acid.—A mixture of 6.4 g. of ethyl allyl acetonal and 0.04 g. of *p*-toluenesulfonic acid was heated as in the previous experiment. Five grams of material was collected while the bath temperature was raised slowly from 120 to 180°. The distillate was shaken with 50 cc. of distilled water, and the resulting upper layer washed twice with 10-cc. portions of water before drying over anhydrous potassium carbonate. After filtering, the material was distilled in a 2-cc. modified Claisen distilling flask at atmospheric pressure.

Fraction	B. p., °C.	Wt., g.	$n^{20}\text{D}$
1	82–88	0.10	..
2	88–90	.53	1.4155
Residue	..	.24	..

This distillate was chiefly α-methylvinyl allyl ether.

α-Chloro-β-bromoethyl Allyl Ether.—To 43.7 g. of a mixture of bromoacetaldehyde and tribromoparaldehyde at 0° was added 20.6 g. of dry allyl alcohol. At this temperature, dry hydrogen chloride was introduced with constant stirring until a 17.5 g. increase in weight was noted. At the end of the reaction two colorless layers had formed. The lower one was placed over anhydrous calcium chloride and the excess hydrogen chloride was evaporated under reduced pressure. A light-brown color appeared after standing for two days. After filtering, the α-chloro-β-bromoethyl allyl ether weighed 44 g. (62% yield).

In another run crystals of tribromoparaldehyde settled out during the reaction. The yield in this case (59.3%) was based on the unrecovered aldehyde.

α-Phenyl-β-bromoethyl Allyl Ether.—Phenylmagnesium bromide was prepared in the usual way from 176 g. (1.12 moles) of bromobenzene, 27 g. of magnesium and 400

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[13] Palomaa and Kenetti, *Ber.*, **64**, 799 (1931).

[14] Von Braun and Stechele, *ibid.*, **33**, 1472 (1900).

cc. of dry ether. After cooling to 0°, a 1:1 dry ether solution of 134 g. of α-chloro-β-bromoethyl allyl ether was added with constant stirring. The material was added slowly enough so that the mixture remained cold. After the reaction was over, stirring at 0° was continued for twenty minutes before hydrolyzing with dilute hydrochloric acid. The ether layer was separated and dried over anhydrous calcium chloride.

After filtering, the ether was distilled off on the steam-bath, 3.5 g. of solid sodium hydroxide was added and the residue distilled under reduced pressure. Sixty-six grams (41% yield) of α-phenyl-β-bromoethyl allyl ether was obtained, distilling between 130–142° at 18–21 mm. Several refractionations were necessary in order to obtain a pure product, b. p. 129–130° (12 mm.). The major impurity was diphenyl.

Anal. Calcd. for $C_{11}H_{13}OBr$: Br, 33.16. Found: Br, 32.99. *Analysis* for unsaturation.[15] Subs., 0.2623; cc. of 0.5017 *N* $KBrO_3$–KBr soln. added, 6.43. Cc. of 0.1768 *N* $Na_2S_2O_3$ req. to back-titrate, 5.54. Double bonds per molecule, 1.03.

α-Phenylvinyl Allyl Ether.—To 18 g. of α-phenyl-β-bromoethyl allyl ether in a small distilling flask was added 4.5 g. of finely-powdered potassium hydroxide and the mixture allowed to stand for two hours. Heat was evolved during the addition and a red-brown color was developed. The system was placed under a pressure of 4 mm. and the bath was slowly heated up until gentle refluxing occurred. After one-half hour's refluxing, distillation was permitted to occur and 9 g. of material was collected. Since this gave a positive test for bromine in the sodium fusion test, it was treated further with 1.7 g. of finely powdered potassium hydroxide in a 12-cc. distilling flask. Under a pressure of 12 mm., the material was slowly heated up to refluxing, and maintained for one-half hour. Upon distillation, it was found that the entire distillate (3 g. or 25% yield) came over at 104–105° (12 mm.). A very small amount of water was collected also. The distillate was dried over anhydrous sodium sulfate and filtered therefrom. This unsaturated, colorless liquid gave no halogen test when fused with sodium.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.45; H, 7.56. Found: C, 82.01; H, 7.36.

Acid Hydrolysis of Vinyl Ethers

Vinyl Allyl Ether.—A few drops of vinyl allyl ether was dissolved in 5 cc. of 95% alcohol and two drops of concentrated hydrochloric acid was then added in order to hydrolyze the ether. After the addition of 5 cc. of a saturated solution of 2,4-dinitrophenylhydrazine in 95% alcohol, the mixture was boiled for one minute. Water was added to incipient cloudiness, and the hydrazone was permitted to crystallize. After two recrystallizations, the melting point of the orange crystals was 164–164.5°. A mixed melting point with authentic acetaldehyde 2,4-dinitrophenylhydrazone (m. p. 166°) showed the two materials to be identical (mixed m. p., 165–165.5°). A mixed melting point with the corresponding formaldehyde derivative (m. p. 165°) gave a thirty-degree depression.

α-Methylvinyl Allyl Ether.—This ether was treated in an identical manner. The 2,4-dinitrophenylhydrazone, after two crystallizations from alcohol, melted at 125°. The mixture m. p. with authentic acetone 2,4-dinitrophenylhydrazone (m. p. 125°) was 125°.

α-Phenylvinyl Allyl Ether.—A small amount of the ether was dissolved in dilute alcohol and semicarbazide hydrochloride was added. After gentle heating, the semicarbazone was permitted to form. The melting point, after one recrystallization from dilute alcohol, was 198–199°. A mixed melting point (199–200°) with authentic acetophenone semicarbazone (m. p. 200–201°) showed these two materials to be identical.

Pyrolysis of the Ethers

Vinyl Allyl Ether.—The method used here consisted in passing the vapors of the ether through a tube (16 × 0.7 cm.) which was heated to a constant temperature by the refluxing vapors of a proper bath material.

When naphthalene was used to provide a temperature of 215–218°, no rearrangement was observed. When 6.7 g. of vinyl allyl ether was passed through the tube during a period of twenty minutes, the 6.5 g. of recovered material proved to be unchanged ether.

When phenyl ether (b. p. 252–255°) was used, however, definite rearrangement was observed.

Run	Ether used, g.	Product	Time of run, min.
1	3.92	3.64	50
2	11.0	10.6	115

In these runs, 40–50% of a higher-boiling substance (b. p. 99–104°) was isolated from the recovered material, while the rest proved to be unreacted vinyl allyl ether. After several refractionations, 2.5 g. (approx. 50% of the combined fractions, b. p. 99–104°) came over constantly between 103–104° (749 mm.). This material had a pungent aldehyde-like odor and reacted immediately with Schiff's reagent. It was found to be much more soluble than vinyl allyl ether upon shaking with water. This fraction had the following constants: d^{20}_4 0.852; n^{20}_D 1.4191.

Anal. Calcd. for C_5H_8O: C, 71.38; H, 9.59. Found: C, 70.99, 71.08; H, 9.53.

The dimethone[16] derivative of allylacetaldehyde was prepared, and melted sharply at 98° after several recrystallizations from alcohol.

Anal. Calcd. for $C_{21}H_{30}O_4$: C, 72.79; H, 8.73. Found: C, 72.94; H, 8.62.

The 2,4-dinitrophenylhydrazone of allylacetaldehyde also was prepared. After three recrystallizations from alcohol, the melting point remained unchanged at 120°.

α-Methylvinyl Allyl Ether.—The same apparatus was used as in the case of vinyl allyl ether. The vapors of 3.6 g. of α-methylvinyl allyl ether were passed through the tube, which was heated to 255° by the refluxing vapors of phenyl ether, during the course of one hour. Three and three-tenths grams of material was recovered. On distillation, practically all of this distilled at 126–127° at 745 mm. Properties of allylacetone: n^{20}_D 1.4199; d^{20}_4 0.842; *MR* (found) 29.47, *MR* (calcd.) 29.45.

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(15) Davis, Crandall and Higbee, *Ind. Eng. Chem., Anal. Ed.*, **3**, 108 (1931).

(16) Klein and Linser, *Mikrochemie*, Pregl Festschrift, 204 (1929). "Methone" is a trade name for dimethyldihydroresorcinol.

The presence of the CH_3CO– group was indicated by the good iodoform test obtained from a drop of this material. Preparation of the semicarbazone (m. p. 103°) and the 2,4-dinitrophenylhydrazone[17] (m. p. 108–108.5°) further confirmed its identity.

α-Phenylvinyl Allyl Ether.—When 1.31 g. of this ether was refluxed gently under atmospheric pressure for fifteen minutes, a red-brown color developed. After cooling, the system was distilled at 12–13 mm. The entire volatile portion (0.93 g.) came over between 105–116°. A small amount of a deep red-brown, viscous material remained as residue. The refractive index $n^{20}{}_D$ of the distillate was 1.5417.

The semicarbazone was prepared in the usual manner and found to melt, after two recrystallizations, at 156–157°. The oxime was also recrystallized twice and had the melting point of 53°.[18] A mixed m. p. with a sample of authentic acetophenone oxime (m. p. 57–58°) showed definitely that these two materials were different. Simple mixing gave a sticky mass, which was completely melted at 45.5°. This distillate is, therefore, identified as γ-butenyl phenyl ketone.

Ozonolysis of Allylacetaldehyde.—One gram of allylacetaldehyde was dissolved in 100 cc. of dry carbon tetrachloride and an excess of a 5% ozone-in-oxygen stream passed into the solution at 0°. The resulting ozonide was hydrolyzed in the presence of the solvent with 70 cc. of water and the reaction completed by refluxing for one and one-half hours. At this point, the freshly-prepared and well-washed silver oxide from 15 g. of silver nitrate was added and the mixture was further refluxed for one hour. After the evaporation of the carbon tetrachloride by gentle heating on the steam-bath, the mixture was filtered.

Most of this filtrate was distilled, the distillate made up to 110 cc., and a determination of the Duclaux values made.

	Cc. alkali required
Original 10 cc.	2.90
First 10 cc. distilled	1.20
Second 10 cc. distilled	1.30
Third 10 cc. distilled	1.40

Duclaux values found: 4.14, 4.48, 4.83. The theoretical values for formic acid are: 3.95, 4.40 4.55. This distillate slowly decolorized potassium permanganate solution.

After the formic acid had been distilled off, the residue was treated with excess of hydrochloric acid to precipitate the remaining silver. After filtering, the filtrate was evaporated to dryness.

A small amount of this residue was dissolved in water and neutralized with dilute sodium hydroxide. The *p*-bromophenacyl ester of the acid was prepared in the usual manner and was recrystallized from an alcohol–acetone mixture; m. p. 209–210°. A mixed melting point with authentic *p*-bromophenacyl succinate (m. p. 213.5–214°) showed the identity of the two materials. The value was 212–212.5°.

Summary

A number of methods of preparing vinyl allyl ethers have been investigated.

These ethers were found to rearrange smoothly upon heating at temperatures of 175–255°. Only one product was found to any appreciable extent in each case, indicating a clean-cut reaction. It was shown that allylacetaldehyde, allylacetone, and ω-allylacetophenone were formed in this way, respectively, from vinyl allyl ether, α-methyl vinyl allyl ether, and α-phenylvinyl allyl ether. These three ethers are listed in the order of decreasing thermal stability.

The rearrangement of vinyl allyl ether to allylacetaldehyde is analogous to the rearrangement of phenyl allyl ether to *o*-allylphenol.

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[17] Allen, THIS JOURNAL, **52**, 2958 (1930), reports m. p. of 104°

[18] Helferich and Lecher, *Ber.*, **54**, 930 (1921), report the m. p. of the semicarbazone of γ-butenyl phenyl ketone as being 156–157°, and that of the oxime as 53–54°.

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Polycondensation of Acrolein

BY EVERETT E. GILBERT[1] AND JOHN J. DONLEAVY

It has been shown[2] that in the presence of dilute aqueous alkalies, α-methylacrolein polycondenses by a Michael mechanism to yield hydroxy polyaldehydes. The purpose of this communication is to report a similar reaction for acrolein.

Several investigators have recorded the precipitation of a white solid upon the addition of alkalies to an aqueous solution of acrolein. McLeod[3] obtained a product softening at 83° and decomposing with evolution of gas at 94–95°. The substance was soluble in alcohol, but insoluble in water and in hydrocarbon type solvents. Upon heating, thermal depolymerization occurred with the formation of acrolein. Another observer[4] obtained a white powder softening at

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[1] This communication describes work done by Everett E. Gilbert in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Gilbert and Donleavy, THIS JOURNAL, **60**, 1737 (1938).

[3] McLeod, *Am. Chem. J.*, **37**, 34 (1907).

[4] Nef, *Ann.*, **335**, 220 (1904).