hours, and then distilled slowly to yield 90 g. of a liquid, b.p. 115–145°. This distillate was washed once with 130 ml. of 20% sodium carbonate solution and twice with 25-ml. portions of the same solution. After being dried over anhydrous sodium carbonate, the remaining 60.1 g. of liquid was distilled over solid potassium hydroxide to yield 57 g. of liquid, b.p. 138–148°, which when fractionated gave 54 g. of 1-hexenyl ethyl ether, b.p. 144–147°, n_D^{25} 1.4160, d_4^{25}

0.7915. The yield was 84.4% based on 1-ethoxyhexyl acetate and 49% based on hexanal.

The infrared spectrum of compound (IIIb) exhibited prominent absorption bands at 3.46(s), 6.02(s), 6.83(m), 7.22(s), 7.34(m), 7.67(m), 7.94(m), 8.07(m), 8.26(s), 8.49(s), 9.02(s), 10.71(m), 12.67(s) microns.
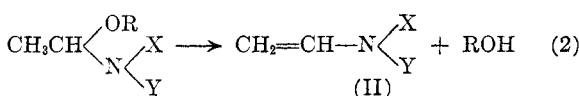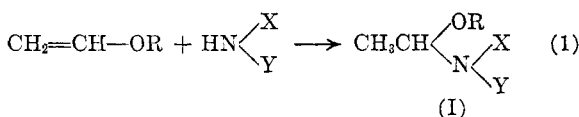
BATON ROUGE 3, LA.

Reaction of Vinyl Ethers with Acidic Imino Compounds. A New Synthesis of Some N-Vinyl Imides

JUNJI FURUKAWA, AKIRA ONISHI, AND TEIJI TSURUTA

By heating vinyl ethers with dicarboxylic acid imides, there were formed addition products which were proved to be x-imidoethers. With N-methyl-p-toluenesulfonamide as a reactant, the adduct formation did not occur until an acidic catalyst was added to the reaction system. N-Vinylimides were prepared by elimination of alcohol, with the aid of an acidic catalyst, from the corresponding α-imidoethers. In the case of N-α-butoxyethyl-N-methyl-p-toluenesulfonamide, the elimination took place without any added catalyst to give N-methyl-N-vinyl-p-toluenesulfonamide.

In the course of our studies on organic syntheses with vinyl ethers as starting materials, these compounds were found to react readily with some acidic imides to give α-imidoethers (I), from which N-vinylimides (II) could be prepared by elimination of alcohol with the aid of acidic catalysts.

$$\text{CH}_2\!\!=\!\!\text{CH}\!-\!\text{OR} + \text{HN}\!\!<_Y^X \longrightarrow \text{CH}_3\text{CH}\!\!<_{N<_Y^X}^{OR} \quad (1)$$
$$(\text{I})$$

$$\text{CH}_3\text{CH}\!\!<_{N<_Y^X}^{OR} \longrightarrow \text{CH}_2\!\!=\!\!\text{CH}\!-\!\text{N}\!\!<_Y^X + \text{ROH} \quad (2)$$
$$(\text{II})$$

This paper examines the reactivity of these imides and certain amides in the addition reaction. Details of methods for preparing N-vinylimides are also reported.

The addition reaction. With dicarboxylic acid imides, the addition reaction (1) was done by heating the reaction mixture without any added catalysts. Under similar reaction conditions, benzamide[1] or p-toluenesulfonamide also reacted with vinyl ethers to give ethylidenediamides. N-Methyl-p-toluenesulfonamide, on the other hand, gave an imidoether (I), provided a small quantity of hydrochloric acid was added. Products, yields, and physical properties are given in Table I.

The adducts were readily hydrolyzed by 1:1 hydrochloric acid to give acetaldehyde, the corresponding alcohol, and the dicarboxylic acid, its imide, or the amide. The addition products therefore have α-imido-ether and ethylidenebisamide

structures, since β-adducts would not give acetaldehyde on hydrolysis. Since Voronkov[1] reported that ethylidenediacylamides have the structure (III), the alkoxyethyl dicarboxylic imides could have a similar structure (IV). However, as will be described later, N-vinylphthalimide was formed by the elimination of alcohol from α-ethoxyethylphthalimide. Thus, structure (IV) can be eliminated[2] in favor of V.
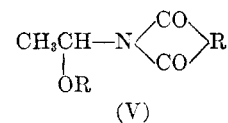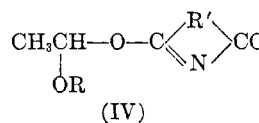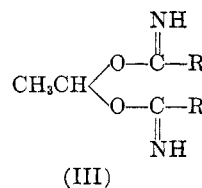
From experiments to determine the optimum condition for the preparation of N-α-butoxyethylsuccinimide, it was found that the optimum condition (100% conversion and 94–95% yield) is as follows: reaction temperature, 195°; reaction time, 3–5 hours; and the molar ratio of succinimide to vinyl ether, 1:2 or 3:4. Results as to the other N-α-alkoxyethyldicarboxylic acid imides are listed in Table II.

In the reaction of butyl vinyl ether with benzamide, we observed that benzamide crystals gradually disappeared on heating, and finally resulted in a clear solution; but, on prolonged heating,

---

(1) Voronkov reported addition reactions between vinyl ether and some acylamides. M. G. Voronkov, *J. Gen. Chem. (U.S.S.R.)*, **21**, 1631 (1951); *Chem. Abstr.*, **46**, 8002 (1952).

(2) Ethylidenedibenzamide, (C₆H₅CONH)₂CHCH₃, is also reported. British Patent **710,468**; *Chem. Abstr.*, **49**, 11709 (1955).

TABLE I

α-IMIDOETHERS, α-IMINOETHER AND ETHYLIDENEDIAMIDES

Compound	Yield,[a] %	M.P., °C.	Formula	Analysis C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found
N-α-Ethoxyethylsuccinimide	93	124–125 (8 mm.)[b]	$C_8H_{13}O_3N$	56.12	56.26	7.65	7.50	8.18	7.91
N-α-Butoxyethylsuccinimide	95	135–138 (9 mm.)[c]	$C_{10}H_{17}O_3N$	60.28	60.51	8.60	8.78	7.03	7.04
N-α-Phenoxyethylsuccinimide	79	77.5–78.5[d]	$C_{12}H_{13}O_3N$	65.74	65.99	5.98	6.02	6.39	6.42
N-α-Ethoxyethylphthalimide	82	63–65[e]	$C_{12}H_{13}O_3N$	65.74	65.92	5.98	5.52	6.39	6.82
N-α-Phenoxyethylphthalimide	41	92.5–93.5[e]	$C_{16}H_{13}O_3N$	71.90	72.18	4.90	5.03	5.24	5.15
N-α-Butoxyethylglutarimide	91	145–146 (5 mm.)[f]	$C_{11}H_{19}O_3N$	61.94	61.18[g]	8.98	8.94	6.62	6.90
N-α-Ethoxyethylcarbazole	54	74–74.5	$C_{16}H_{17}ON$	80.30	80.08	7.16	7.01	5.85	5.57
N-α-Butoxyethyl-N-methyl-p-toluenesulfonamide	84	160–164 (4 mm.)[h]	$C_{14}H_{23}O_3NS$	58.91	58.91	8.13	7.67	4.91	5.47[i]
Ethylidenedibenzamide	63	203–205	$C_{16}H_{16}O_2N_2$	71.62	71.49	6.01	5.92	10.44	10.19
Ethylidenedi-p-toluene-sulfonamide	11	110–114 dec.	$C_{16}H_{20}O_4N_2S_2$	52.15	52.65	5.47	5.57	7.60	7.29

[a] Based upon unrecovered imide, amide, or carbazole. [b] Boiling point of liquid adduct. [c] Boiling point of liquid adduct; n_D^{20} 1.4678, d_4^{20} 1.069. The crude product was washed three times with water, dried over sodium sulfate, and redistilled. [d] Recrystallized once from alcohol and then three times from the mixture of benzene and petroleum benzine. [e] Recrystallized from alcohol. [f] Boiling point of liquid adduct; n_D^{17} 1.4750. The crude fraction was dissolved in petroleum ether and filtered. The filtrate was redistilled under nitrogen. [g] The analysis was unsatisfactory owing to slight decomposition, but on hydrolyzing with 1:1 hydrochloric acid the adduct gave acetaldehyde in almost quantitative yield. [h] Boiling point of liquid adduct. Distillation was carried out under nitrogen. [i] The analysis was unsatisfactory owing to the slight decomposition, but the results of hydrolysis and elimination of alcohol support this structure.

TABLE II

PREPARATIONS OF SOME N-α-ALKOXYETHYL-DICARBOXYLIC ACID IMIDES

Product	Reactant Moles of Imide	Moles of Vinyl Ether	Temp., °C.	T, Hr.	Yield,[a] %
N-α-Ethoxyethylsuccinimide	2	5	160	7	93
N-α-Phenoxyethylsuccinimide[b]	0.1	0.15	260	4.5	79
N-α-Ethoxyethylphthalimide[c]	0.75	3.0	160	9	82
N-α-Phenoxyethylphthalimide[d]	0.1	0.15	260	2	41
N-α-Butoxyethylglutarimide[e]	0.3	1.5	220	6	91

[a] Based upon the reacted succinimide. [b] Reactants were diluted with 20 ml. of benzene. [c] Isolated after vinyl ether and acetal were removed from the reaction mixture by cooling the residue and collecting the crystals. [d] Reactants were diluted with 20 ml. of benzene. The mixture was distilled under reduced pressure, and the fraction, b.p. 170–205° (3 mm.), allowed to crystallize with cooling; the solidified fraction was pressed on a clay plate. Conversion 72%. [e] Conversion 56%.
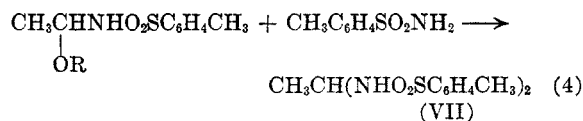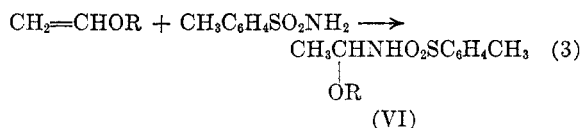
white crystals reappeared and increased in quantity. The latter crystals were proved to be ethylidene-dibenzamide. The formation of α-butoxyethyl-benzamide as an intermediate may be supposed from these observations. However, an attempt to isolate the intermediate by vacuum distillation failed because of its instability.

An *N*-alkyl acylamide (*N*-methylacetamide), *N*-aryl acylamide (acetanilide, benzanilide, *p*-nitroacetanilide), ε-caprolactam and phenanthridone did not react even at temperatures as high as 200–220°.

As shown in Table I, carbazole added to ethyl vinyl ether, but indole and acridone gave only resinous substances and diphenylamine did not react under the conditions.

p-Toluenesulfonamide reacted with phenyl vinyl ether in the presence of concentrated hydrochloric acid to give ethylidenedi-*p*-toluenesulfonamide (VII). Even without the catalyst, reaction with *n*-butyl vinyl ether took place, but the product, which was obtained as white crystals, decomposed

to the starting amide on further purification. Presumably, this may be the amidoether (VI). The formation of ethylidenedi-*p*-toluenesulfonamide is considered to occur in the same way as the carboxylic acid amide.

$$CH_2{=}CHOR + CH_3C_6H_4SO_2NH_2 \longrightarrow$$
$$CH_3CHNHO_2SC_6H_4CH_3 \quad (3)$$
$$\mid$$
$$OR$$
$$(VI)$$

$$CH_3CHNHO_2SC_6H_4CH_3 + CH_3C_6H_4SO_2NH_2 \longrightarrow$$
$$\mid$$
$$OR$$
$$CH_3CH(NHO_2SC_6H_4CH_3)_2 \quad (4)$$
$$(VII)$$

N-Methyl-*p*-toluenesulfonamide also reacted with *n*-butyl vinyl ether in the presence of concentrated hydrochloric acid to give an 84% yield of *N*-methyl - *N* - α - butoxyethyl - *p* - toluenesulfon-amide (VIII).

TABLE III

ELIMINATION OF ALCOHOL FROM α-IMIDOETHERS

α-Imidoether	Method	Catalyst	Conversion (%)	Yield[a] (%)
N-α-Ethoxyethylsuccinimide	B	NaHSO₄·H₂O	100	69
N-α-Ethoxyethylsuccinimide	A	NaHSO₄·H₂O	Produced resins	—
N-α-Butoxyethylsuccinimide	B	NaHSO₄·H₂O	60–90	76
N-α-Butoxyethylsuccinimide	B	KHSO₄	67	61
N-α-Butoxyethylsuccinimide	B	P₂O₅	73	60
N-α-Butoxyethylsuccinimide	B	H₂N·C₆H₄·SO₃H	0	0
N-α-Butoxyethylsuccinimide	B	H₂SO₄	79	76
N-α-Ethoxyethylphthalimide	B	NaHSO₄·H₂O	100	26
N-α-Ethoxyethylphthalimide	A	NaHSO₄·H₂O	100	65
N-α-Ethoxyethylcarbazole	B	NaHSO₄·H₂O	100	0
N-α-Ethoxyethylcarbazole	A	H₂N·C₆H₄·SO₃H	88	0

[a] Based upon the reacted succinimide.

$$CH_3CHN(CH_3)O_2SC_6H_4CH_3$$
$$|$$
$$OC_4H_9$$

(VIII)
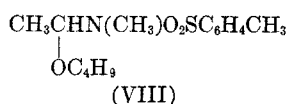
However, this was not so stable as products from dicarboxylic acid imides, so distillation was accompanied by slight decomposition. Even without catalyst, saccharin reacted quite readily with n-butyl vinyl ether, but the product was too unstable to be isolated.

From the results described above, it may be seen that -NH-group which can add to vinyl ether are loosely classified into acidic imides, amides, and imine. The sulfonyl or carbonyl group attached to the nitrogen atom seems to increase the reactivity of the amine. The pyrrole ring has also a weaker activating effect.

Preparation of N-vinylimides. The direct preparation of N-vinyldicarboxylic acid imides has been caried out by the reaction between acetylene and dicarboxylic acid imides in the presence of mercuric salts[3] or cadmium acetate[4] as catalyst under pressure, and by a vapor phase reaction using catalysts such as zinc oxide or cadmium oxide.[5] These methods are not satisfactory from a point of view of reaction rate or conversion. As to the indirect method, Yoshida and Hirakawa[6] reported the preparation of N-vinylphthalimide from vinyl acetate and phthalimide. Hanford and Stevenson[7] reported the preparation and polymerization of N-vinylsuccinimide and other aliphatic vinyl tertiary amides. We therefore tried to prepare N-vinylimides by elimination of alcohol from the α-imidoethers which were obtained through the above method.

Elimination of alcohol from the imidoether was

carried out by heating a mixture of imidoether and catalyst. After the reaction, the catalyst was made inactive and the N-vinylimide formed was separated by chilling or distillation (Method A). This method was suitable for the preparation of N-vinyl imides which were relatively stable to the catalyst and heat, such as N-vinylphthalimide. However, in the case of unstable N-vinylimides such as N-vinylsuccinimide, the elimination reaction and the distillation were simultaneously carried out (Method B).

In Table III are listed the catalysts used and a comparison of Methods A and B.

In the elimination of butanol from N-α-butoxyethylsuccinimide by Method B, it is shown that sodium bisulfate and sulfuric acid are most effective catalysts. Since sodium bisulfate does not have so strong an effect, the poor reproducibility of the results may be ascribed to the heterogeneity of the reaction mixture. With sulfuric acid as catalyst, reaction was rapid and the results were reproducible, but the effect was so strong that careful control of the reaction conditions was required to avoid side reactions. Potassium bisulfate and phosphorus pentoxide were somewhat less effective catalysts.

N-Vinylsuccinimide was prepared by Method B; Method A gave only a resinous substance. Compared with N-vinylsuccinimide, N-vinylphthalimide has a higher boiling point and lower polymerizability, and so Method A gave the better result. Although attempts were also made to prepare N-vinylglutarimide from N-α-butoxyethylglutarimide by both methods, the latter compound was shown to decompose only to glutarimide, but not to N-vinylglutarimide under the conditions.

When N-methyl-N-α-butoxyethyl-p-toluenesulfonamide was distilled at 250–260° under a pressure of 22–30 mm., it was decomposed almost completely to give 1-butanol and N-vinyl-N-methyl-p-toluenesulfonamide in 74% yield based upon the reacted sulfonamide. Attempts to prepare N-vinylcarbazole from the corresponding imidoether failed.

(3) R. F. Conaway, U. S. Patent 2,231,887; *Chem. Abstr.*, 35, 3266 (1941).

(4) A. Onishi and J. Furukawa, *J. Soc. Organic Synthetic Chem. Japan*, 9, 69 (1951).

(5) S. Akiyoshi, T. Matsuda, and J. Murata, *J. Chem. Soc. Japan, Ind. Chem. Section*, 56, 440 (1953).

(6) T. Yoshida and H. Hirakawa, *J. Chem. Soc. Japan, Ind. Chem. Section*, 55, 83 (1952).

(7) W. E. Hanford and H. B. Stevenson, U. S. Patent 2,231,905; *Chem. Abstr.*, 35, 3267 (1941).

EXPERIMENTAL

Reaction of dicarboxylic acid imides with vinyl ethers. In a stainless steel rocking autoclave were placed dicarboxylic acid imide, an excess of vinyl ether, and 0.2–1.0 g. of hydroquinone. The autoclave was flushed with nitrogen and then heated. The temperature and the time of reaction are listed in Table II. After the reaction, the autoclave was allowed to cool to room temperature and opened. The unreacted imide was removed by filtration (followed by washing with water, if necessary, such as in the case of succinimide). Then vinyl ether and acetal were stripped off and the residue was submitted to a vacuum-distillation under nitrogen. In the case of phthalimide, recrystallizations of the residue from alcohol gave a better yield. Table I lists the yields and analytical data for these products.

Acid hydrolysis of α-imidoethers derived from dicarboxylic acid imide. A sample of 4–10 g. α-imidoether and 30–40 ml. of 1:1 hydrochloric acid were placed in a flask equipped with inlet and outlet tubes. The mixture was heated to 80° for 2–4 hr. During the period a slow current of nitrogen was passed through in order to remove the last trace of acetaldehyde formed. The acetaldehyde vapor was introduced into ethanol at 0° and converted to 2,4-dinitrophenylhydrazone according to Brady.[8] The hydrazone was recrystallized several times from ethanol, m.p. 164–166.5°, and was identified by a mixture melting point with an authentic sample. Dicarboxylic acid or its imide was obtained in good yield from the reaction mixture by filtration or by evaporating to dryness and then extracting with acetone. Melting points were not depressed by mixing with corresponding authentic samples (phthalimide, m.p. 222–224°; succinic acid, m.p. 186.5–188°; glutaric acid, m.p. 96–97°). Hydrolysis of *N*-α-butoxyethylglutarimide gave acetaldehyde (yield 99%), butanol (yield 25%) and glutaric acid (yield 80%).

N-Vinylsuccinimide[7] from N-α-butoxyethylsuccinimide, Method B. The apparatus consisted of a reactor, a condenser, and two receivers. The reactor was a modified Claisen distillation flask with an additional neck through which a thermometer was dipped into the reaction mixture. The second receiver, which has a coiled glass tube, was chilled with ice-salt mixture. A mixture of 199 g. (1 mole) of *N*-α-butoxyethylsuccinimide and 1.4 g. of powdered sodium bisulfate monohydrate was placed in the reactor. In the case of sulfuric acid catalyst, 0.4 ml. of the acid was placed at the beginning and 0.2 ml. more was added when the reaction rate had dropped considerably. The system was maintained at a pressure of 6–7 mm. and swept with nitrogen for 30 min. When the mixture was heated in an oil bath at 113–120°, vigorous decomposition occurred and 1-butanol and *N*-vinylsuccinimide began to distil. At the end of the reaction, the reaction temperature was elevated to 125–130°. It took 2.5–3.5 hr. to distil over the contents of the flask. The condensate in the second receiver was mainly 1-butanol (b.p. 116–118°; 3,5-dinitrobenzoate, m.p. 62–63°, identification by the mixture melting). To the condensate in the receiver I was added a small amount of hydroquinone, and it was fractionated under nitrogen. There was obtained a small amount of 1-butanol and the following fractions: (*1*) b.p. 96–111° (7.5 mm.), (*2*) b.p. 111–125° (7.5 mm.), (*3*) b.p. 125–132° (7.5 mm.). The first fraction was crystallized from ether, m.p. 48–49° (*N*-vinylsuccinimide).

Anal. Calcd. for $C_6H_7NO_2$: C, 57.59; H, 5.64; N, 11.19. Found: C, 57.65; H, 5.52; N, 11.03.

The third fraction was a mixture of unreacted butoxyethylsuccinimide and succinimide. They were separated by filtration. The results are listed in Table III. Similar reaction conditions were employed in the case of the other catalysts.

Method A: When the above reaction mixture was heated

(8) O. L. Brady, *J. Chem. Soc.*, 757 (1931).

at 113–120° for 3 hr. without simultaneous distillation of the products during the reaction, the contents were resinified and *N*-vinylsuccinimide could not be obtained on distillation.

N-Vinylsuccinimide from N-α-ethoxyethylsuccinimide, Method B. The elimination of alcohol from *N*-α-ethoxyethylsuccinimide (48.9 g., 0.29 mole) was carried out in a similar way. *N*-Vinylsuccinimide was isolated by chilling the distillate to −73° in a Dry Ice–ethanol bath. Twenty-four and seven-tenths grams of crystals were thus obtained (yield 69%), and were recrystallized from alcohol yielding white crystals, m.p. 48–49°. Yield was 18.8 g. (60%). The distillate, condensed in receiver II, was proved to be ethanol.

Acid hydrolysis of *N*-vinylsuccinimide was done in a manner similar to the α-imidoether and gave acetaldehyde in an almost quantitative yield and succinic acid in 76% yield.

N-Vinylphthalimide, Method A. A mixture of 11 g. (0.05 mole) of *N*-α-ethoxyethylphthalimide and 0.2 g. of powdered sodium bisulfate monohydrate was placed in a 100 ml., three-necked flask equipped with a thermometer, gas inlet- and outlet-tube. After the system was swept with nitrogen for 30 min., the mixture was heated at 126° (initial)–143° (final) for 15 min., cooled to room temperature and extracted with ether. Ether was stripped off and the residue was distilled under reduced pressure with a small amount of hydroquinone. A fraction (5.7 g.; 65.1%) of b.p. 119–125° (6.5 mm.), m.p. 77–82° was obtained. Recrystallization from ethanol gave white crystals, m.p. 84°.

Anal. Calcd. for $C_{10}H_7NO_2$: C, 69.34; H, 4.08; N, 8.09. Found: C, 69.47; H, 4.12; N, 7.92.

Elimination of 1-butanol from N-α-butoxyethylglutarimide. Sodium bisulfate monohydrate (0.1 g.) was added to 10 g. of *N*-α-butoxyethylglutarimide and the mixture was treated according to Method B at 136–139° under reduced pressure of 8 mm. Hg. A small amount (1.5 g., 28%) of glutarimide was obtained by chilling the distillate.

Ethylidenedibenzamide. A mixture of 1 g. (0.008 mole) of benzamide and 3 g. (0.025 mole) of phenyl vinyl ether was refluxed gently for 2 hr. After cooling to room temperature, the precipitates were filtered and recrystallized from benzene, m.p. 137–157°; yield 0.7 g. (63%) of crude ethylidenedibenzamide. After four successive recrystallizations from benzene, the melting point was raised to 203–205°.

Reaction of benzamide with n-butyl vinyl ether. A mixture of 60 g. (0.5 mole) of benzamide, 200 g. (2 moles) of *n*-butyl vinyl ether and 0.5 g. of hydroquinone was heated in an oil bath at 110°. The crystals of benzamide disappeared gradually to give a clear solution. After heating for 10 hr., white crystals began to deposit. The crystals were filtered (10.8 g.) and recrystallized from benzene, m.p. 202–204°. They were identified by mixture melting with an authentic sample of ethylidenedibenzamide. Dibutyl acetal (66.8 g.) and unreacted vinyl ether were removed from the filtrate. The remaining residue (102 g.) could not be distilled without decomposition even *in vacuo* and under nitrogen. The distillate (79 g.) was composed of 1-butanol and a liquid, b.p. 165–192° (4.2 mm.), which was distilled twice at reduced pressure to yield an unknown material, b.p. 182–186° (3 mm.), having the following elementary composition.

Anal. Found: C, 71.72; H, 8.56; N, 5.43.

Reaction of p-toluenesulfonamide with n-butyl vinyl ether. When a mixture of *p*-toluenesulfonamide and *n*-butyl vinyl ether was heated at 110°, a clear solution was obtained after 5–10 min. After cooling to room temperature, the precipitates were filtered and dried. The precipitates were found not to be *p*-toluenesulfonamide by their m.p. (70–74°) and mixture melting, but the identification of their structure failed because they were too unstable to be isolated in pure state.

Ethylidenedi-p-toluenesulfonamide. A mixture of 8.5 g. (0.05 mole) of *p*-toluenesulfonamide, 12 g. (0.1 mole) of phenyl vinyl ether and two drops of concentrated hydrochloric acid was heated on a steam bath. The crystals of *p*-toluenesulfonamide disappeared after 15 min. to give an

orange solution. Heating was stopped after 20 min., the mixture was cooled to room temperature, and the precipitates were filtered. The precipitates were heated with 20 ml. of benzene and filtered hot with suction. Insoluble matter was washed with benzene and dried, m.p. 115–117°, yield, 1 g. (11%). After five successive crystallizations from benzene, white needles melting with decomposition at 110–114° were obtained.

The acid hydrolysis of ethylenedi-p-toluenesulfonamide was worked up as described previously. Acetaldehyde 2,4-dinitrophenylhydrazone and p-toluenesulfonamide (85.8%) were obtained.

N-α-Butoxyethyl-N-methyl-p-toluenesulfonamide (IX). A mixture of 111 g. (0.6 mole) of N-methyl-p-toluenesulfonamide, 240 g. (2.4 moles) of n-butyl vinyl ether and 0.6 ml. of concentrated hydrochloric acid was heated at 60° for 2.5 hr., allowed to cool, washed successively with 5% sodium hydroxide solution and water, and dried over sodium sulfate overnight. Vacuum distillation under nitrogen yielded 144.2 g. (84%) of product, b.p. 162–184° (5.5 mm.). During the distillation, slight decomposition was observed. An analytical sample was prepared by redistillation, b.p. 160–164° (4 mm.).

The same procedure was used for the acid hydrolysis of (IX) as described previously. Acetaldehyde 2,4-dinitrophenylhydrazone (91%) and N-methyl-p-toluenesulfonamide (77%) were identified.

N-Vinyl-N-methyl-p-toluenesulfonamide. A sample of 144 g. (0.505 mole) of N-α-butoxyethyl-N-methyl-p-toluenesulfonamide was heated in a Claisen flask under a pressure

of 22–30 mm. The bath temperature was maintained at 250–260°. The imidoether distilled with decomposition to give 1-butanol and a yellow, oily fraction, b.p. 196–198° (22–30 mm.). Redistillation of the oil yielded 93 g. (87%) of crude product, b.p. 150–157° (4 mm.), which was recrystallized from petroleum ether-benzene to give white crystals, m.p. 56–57.7°.

Anal. Calcd. for $C_{10}H_{13}O_2NS$: C, 56.84; H, 6.20; N, 6.63. Found: C, 56.92; H, 6.31; N, 6.57.

Polymerization. N-Vinyl-N-methyl-p-toluenesulfonamide was heated with 2% benzoylperoxide for 7 hr. on a boiling water bath, but failed to polymerize. On the other hand, when a few drops of an ether solution of boron trifluoride etherate were added to an ether solution of the vinyl sulfonamide, a white polymer deposited, which was insoluble in ether, acetone, and benzene.

N-α-Ethoxyethylcarbazole. A 13.4 g. (0.08 mole) sample of carbazole was treated with 34.6 g. (0.48 mole) of ethyl vinyl ether for 5 hr. at 180° by the same procedure as in the case of dicarboxylic acid imide. There was obtained 8.8 g. (54%) of crude product, b.p. 163–169° (3 mm.). After recrystallization from ethanol, it melted at 74–74.5°.

Pyrolysis of Organic Carbonates

J. L. R. WILLIAMS, K. R. DUNHAM, AND T. M. LAAKSO

A study of the pyrolysis of organic carbonates in a flow system has been carried out to determine the utility of the reaction for the introduction of unsaturation into aliphatic chains.

A comparison of the ease of decomposition of ethyl carbonates and acetates of α-phenethyl alcohol and β-phenethyl alcohol has indicated that the four esters can be arranged into the following order of pyrolytic instability: 300°: β-acetate ≃ β-carbonate ≃ α-acetate ≃ α-carbonate; 400°: β-acetate < β-carbonate < α-acetate < α-carbonate; 500°: β-acetate < β-carbonate < α-acetate = α-carbonate. Pyrolysis of aliphatic bis(ethyl carbonates) led to the formation of dienes as well as a number of intermediate products.

In another study,[1] the disproportionation of unsymmetrical carbonates to form symmetrical carbonates was studied. Formation of the symmet-

$$2ArOCO_2C_2H_5 \xrightarrow{\text{catalyst}} ArOCO_2Ar + (C_2H_5O)_2CO$$
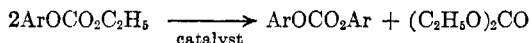
rical carbonates depended on the nature of the group, Ar, and the catalyst.

Ethyl β-phenethyl carbonate underwent a side reaction to form considerable amounts of styrene, rather than the symmetrical carbonate. The catalyzed disproportionations were carried out at 250°, a temperature approaching the range in which esters pyrolyze to form olefins and acids. It was decided to investigate to what extent the formation of styrene was due to the noncatalyzed pyrolysis reaction.

(1) J. L. R. Williams, D. D. Reynolds, K. R. Dunham, and J. F. Tinker, unpublished results.

$$C_6H_5CH_2CH_2O\overset{\displaystyle O}{\overset{\|}{C}}OC_2H_5 \longrightarrow$$
$$C_6H_5CH{=}CH_2 + C_2H_5OH + CO_2$$
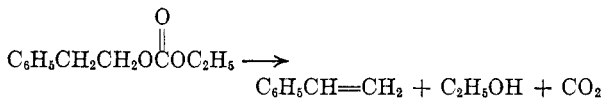
This route is apparently favored over formation of ethylene and β-phenethyl alcohol, since no β-phenethyl alcohol was isolated from the pyrolyses mixtures.

A comparison of acetate and carbonate pyrolyses has been included in this work. It is hoped that carbonic ester pyrolysis will serve as an acid-free pyrolysis system, for use in the preparation of unsaturates bearing acid sensitive functional groups.

A. Pyrolyses of phenethyl alcohol esters. Pyrolyses of the acetates and ethyl carbonates of α-phenethyl alcohol and β-phenethyl alcohol indicate that the carbonate structure undergoes pyrolytic rupture under conditions similar to those used for the acetate unit. Both the α- and β-esters of the two al-