phenyl) by use of 1-cm. cells in the Carey Recording Spectrophotometer. It is noted that the wave lengths of absorption maxima are quite similar for these four compounds and in addition that 1,3-diphenyltetramethyldisiloxane alone has prominent absorption peaks at 247.5 and 265.5 mμ. Table I contains a tabulation of the wave lengths of the absorption maxima for these four compounds.

TABLE I

ABSORPTION MAXIMA FOR PHENYL-CONTAINING SILICONES

	Compound	Wave length of absorption maxima, mμ					
a	1,3-Diphenyltetramethyldisiloxane	247.5	253	259	263	265.5	270
b	2,2-Diphenylhexamethyldisiloxane	248	253	259	263	265	270
c	*cis*-1,3,5-Triphenyltrimethylcyclotrisiloxane	248	253	259	263	270	
d	General Electric Co. methyl phenyl silicone oil	248	253	259	263	270	

Although it was possible to obtain Beer's law plots for isoöctane solutions of any one of these compounds, the quantitative determination of phenyl content by comparison of the absorbency of one compound with that of another, taken as a standard, was unsuccessful. No attempt was made to study the effect of siloxane structure or composition upon these ultraviolet absorption spectra (*e. g.*, the effect of varying the number of phenyl groups per silicon atom).

In addition to the curves obtained for the isoöctane solutions of these phenyl-containing compounds, ultraviolet absorption spectra were obtained also for the following undiluted compounds in 2-cm. cells: hexamethyldisiloxane, octamethylcyclotetrasiloxane, and a linear methylsilicone oil.[3] Table II contains a tabulation of the wave lengths of the absorption peaks for these non-phenyl-containing organosilicon compounds.

TABLE II

ABSORPTION MAXIMA FOR NON-PHENYL-CONTAINING SILICONES

	Compound	Approximate wave length of prominent absorption maxima (mμ)					
a	Hexamethyldisiloxane	247	252	259	261	265	268
b	General Electric Co. 9981-LTNV-40 methyl silicone oil	252	258	261	269		
c	Octamethylcyclotetrasiloxane	246	252	260	268		

The apparent similarity between the absorption curves for the undiluted General Electric 9981-LTNV-40 methyl silicone oil and octamethylcyclotetrasiloxane and the curves obtained for the isoöctane solutions of phenyl-containing silicones would indicate that a phenyl bonded to silicon grouping is present as an impurity. However, the methods of preparation of these materials and the intermediates that are used seemingly preclude the presence of an impurity of this type. A comparison of these absorption curves with those of possible non-silicone impurities does not exclude the presence of a hydrocarbon such as benzene.[4] However, by diluting General Electric 9981-LTNV-40 methylsilicone oil with isoöctane a solution is obtained, the absorption curve of which is coincident with that of the isoöctane blank. This then indicates that if an impurity of either the phenyl silicone or aromatic hydrocarbon type is present, it is present in trace amounts only.

The authors wish to acknowledge the assistance given by Dr. H. W. Alter of the Knolls Atomic Power Laboratory in obtaining the Carey instrument curves.

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[3] General Electric Company 9981-LTNV-40 silicone oil.

[4] Tunnicliff, Brattain and Zumwalt, *Anal. Chem.*, **21**, 890 (1949).

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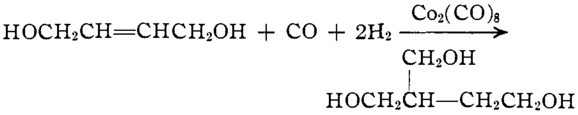
Application of the Oxo Reaction to 2-Butene-1,4-diol

BY L. E. CRAIG, R. M. ELOFSON AND I. J. RESSA

The "oxo" reaction was applied to 2-butene-1,4-diol in hopes of producing a triol (I)



$$HOCH_2CH{=}CHCH_2OH + CO + 2H_2 \xrightarrow{Co_2(CO)_8} HOCH_2\underset{}{\overset{CH_2OH}{\overset{|}{C}}}H{-}CH_2CH_2OH$$

I

However, the main product of the reaction was found to be a rather low boiling alcohol and was presumed to be 3-tetrahydrofurfuryl alcohol formed by the splitting-out of a molecule of water from I. However, the preparation of derivatives of the product suggested that it was 2-tetrahydrofurfuryl alcohol. This was confirmed by mixture melting points of the derivatives with those of an authentic sample of 2-tetrahydrofurfuryl alcohol and by a comparison of the infrared absorption curves of the product and the known alcohol (Fig. 1).

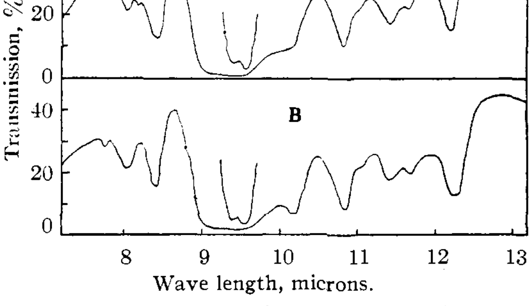
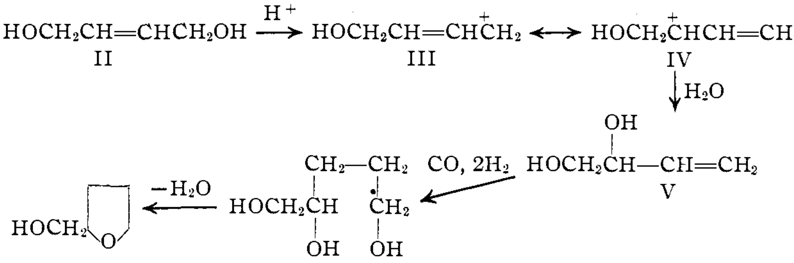


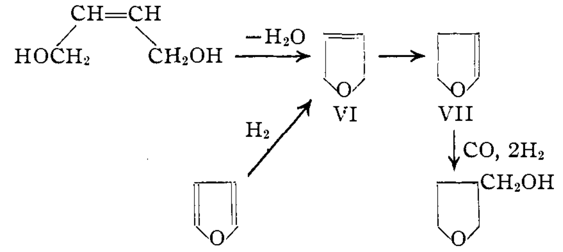
Fig. 1.—Curve A, absorption spectrum of the product of the oxo reaction with 2-butene-1,4-diol; curve B, absorption spectrum of 2-tetrahydrofurfuryl alcohol.

The formation of the unexpected 2-tetrahydrofurfuryl alcohol can be explained by the reactions



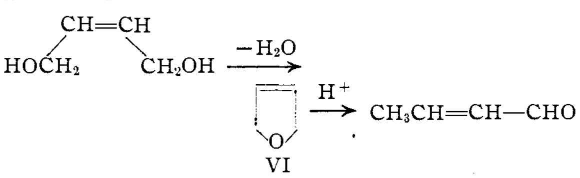
The cobalt tetracarbonylhydride, $Co(CO)_3COH$, formed by the reduction of dicobalt octacarbonyl by hydrogen,[1] could presumably furnish the proton. A similar allylic rearrangement has been proposed to account for the formation of 2-butene-1,4-diol upon hydration of 3,4-epoxy-1-butene.[2] Even though the equilibrium in the second step were in favor of III rather than IV, the carbon monoxide might react with V rather than II because of the more polarized nature of the double bond.

Wender, Levine and Orchin[3] found that the product of the oxo reaction with furan was 2-tetrahydrofurfuryl alcohol. A mechanism which can be suggested to explain the formation of 2-tetrahydrofurfuryl alcohol in both cases is



However, the preparation of VI from furan is unknown; in fact, numerous attempts to hydrogenate furan to a dihydro derivative have failed.[4] Furthermore, VII, which is a vinyl ether, is very sensitive to acid and polymerizes readily with dilute acids.[4]

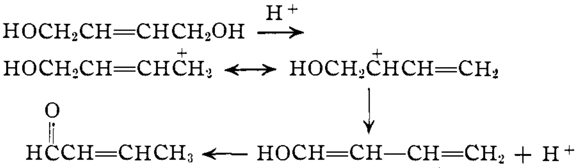
In a reaction which may proceed by a similar mechanism, crotonaldehyde is produced from 2-butene-1,4-diol by treatment with dilute acids. This has been explained by German workers[5] as follows



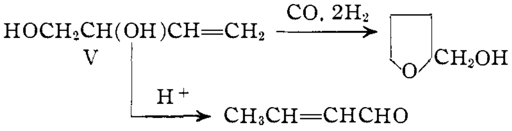
The allylic rearrangement described above could also account for the formation of crotonaldehyde in the manner shown below.

The fact that the *trans* form of 2-butene-1,4-diol does not form VI while the *cis* form does, yet both can be converted to crotonaldehyde,[6] suggests that VI is not formed as the intermediate.

Further evidence for the mechanism involving the allylic rearrangement was



gained by subjecting 3-butene-1,2-diol (V) to the oxo reaction and to treatment with hydrochloric acid. Although much polymerization occurred, 2-tetrahydrofurfuryl alcohol was obtained in the oxo reaction and crotonaldehyde was obtained on treatment with dilute hydrochloric acid.



Experimental

Cobalt Octacarbonyl.—The cobalt octacarbonyl catalyst was prepared by the method of Adkins and Krsek[1] using cobalt or kieselguhr catalyst (Co-0101P) as supplied by the Harshaw Chemical Company of Cleveland, Ohio. The resulting ether solutions contained about 0.05 g. of dicobalt octacarbonyl per ml. of solution.

Oxo Reaction with 2-Butene-1,4-diol.—Into a 400-ml. Aminco bomb were placed 25 g. (0.28 mole) of 2-butene-1,4-diol, 60 ml. of ether and 54 ml. of catalyst solution (about 2.7 g. of dicobalt octacarbonyl). The bomb was purged three times with carbon monoxide at 100 p. s. i., hydrogen introduced to a pressure of 1500 p. s. i., and carbon monoxide added to a total pressure of 3000 p. s. i. The bomb was heated with shaking for six hours at 180°. The pressure during the period of reaction reached a maximum of 4250 p. s. i., dropped to 3600 p. s. i., and then to 2000 p. s. i. when the bomb was cooled to room temperature. After removing the ether by distillation, the residue was distilled *in vacuo* to give, after a small forerun containing water, 12.8 g. of material boiling at 76–82° at 19 mm., $n^{25}\mathrm{D}$ 1.4478. Redistillation through a glass-helices packed column gave colorless liquid, b. p. 69–70° (11 mm.), $n^{25}\mathrm{D}$ 1.4482.

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.82; H, 9.80. Found: C, 58.93; H, 9.89.

The phenylurethan was prepared and crystallized from petroleum ether, m. p. and mixed m. p. with the phenylurethan of an authentic sample of 2-tetrahydrofurfuryl alcohol 56–58°. The 3,5-dinitrobenzoate was prepared and recrystallized from dilute ethanol, m. p. and mixed m. p. with the 3,5-dinitrobenzoate of 2-tetrahydrofurfuryl alcohol 83–84°.

Oxo Reaction with 3-Butene-1,2-diol.—Into a 400-ml. Amino bomb were placed 25 g. (0.28 mole) of 3-butene-

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[1] Adkins and Krsek, This Journal, **70**, 383 (1948).

[2] Bissinger, *et al.*, *ibid.*, **69**, 2955 (1947).

[3] Wender, Levine and Orchin, Abstracts of Papers, 116th Meeting American Chemical Society, Atlantic City, 1949, p. 72.

[4] Private communication from Prof. C. L. Wilson.

[5] P. B. Report No. 606, p. 2.

[6] Valette, *Compt. rend.*, **223**, 907 (1946).

1,2-diol, 90 ml. of ether and 54 ml. of catalyst solution (about 2.7 g. of dicobalt octacarbonyl). The bomb was purged three times with carbon monoxide at 100 p. s. i., hydrogen introduced to a pressure of 1500 p. s. i. and carbon monoxide added to a total pressure of 3000 p. s. i. The bomb was heated with shaking for six hours at 180°. The pressure during the period of reaction reached a maximum of 4000 p. s. i., dropped to 3925 p. s. i. and then to 2250 p. s. i. when the bomb was cooled to room temperature. After removing the ether by distillation, the residue was distilled *in vacuo* to give, after a small forerun containing water, 5 g. of material boiling at 111–117° (30 mm.), $n^{25}\mathrm{D}$ 1.4488. During the distillation, a large amount of residue of polymeric nature formed in the flask.

The 3,5-dinitrobenzoate was prepared and recrystallized from dilute ethanol, m. p. and mixed m. p. with the 3,5-dinitrobenzoate of 2-tetrahydrofurfuryl alcohol 83–84°.

Crotonaldehyde from 3-Butene-1,2-diol.—A mixture of 15 g. (0.17 mole) of 3-butene-1,2-diol and 15 g. of 10% hydrochloric acid in a 100-ml. flask fitted with a short Vigreux column was heated at 100°. The distillate which was a mixture of water and crotonaldehyde amounted to 10.5 g. A black, viscous residue (18.6 g.) remained in the flask. The crotonaldehyde layer was dried and redistilled to give material boiling at 103–105°, $n^{25}\mathrm{D}$ 1.4420; reported b. p. 104–105°, $n^{17}\mathrm{D}$ 1.4384.[7]

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(7) "Handbook of Chemistry and Physics," 30th edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1947.

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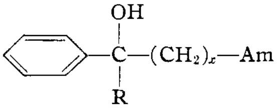
RECEIVED JANUARY 6, 1950

Antispasmodics. V.[1] Tertiary α- and γ-Amino Alcohols and Quaternary Salts of β-Amino Alcohols[1]

BY J. J. DENTON AND VIRGINIA A. LAWSON

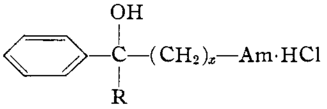
Our previous studies have shown the effect on the antispasmodic activity of variations in chemical structure of the R and Am groups of tertiary β-amino alcohols represented by the following formula (where x is 2 and where R and Am represent various hydrocarbon and disubstituted amino groups, respectively)



To determine further the effect of chemical structure on the antispasmodic activity of compounds of this type, we studied two additional modifications of structure: lower and higher homologs, compounds of the above formula where x is 1 and 3; and quaternary salts of the β-amino alcohols, where x is 2.

β-Amino alcohols, II,[2] V[2,3] and VII[1] in Table I, have been reported previously and were chosen for this study of homologs because they showed a low, medium and high order of antispasmodic activity, respectively. The α-amino alcohols, I and IV in Table I, were prepared essentially by the procedure of Henley,[4] who has described the latter compound. One of the γ-amino alcohols, compound VIII, has been reported by Marxer[5] and by Miescher and Marxer.[6] We have prepared the other two, compounds III and VI in Table I, by a similar procedure.

TABLE I



Number	R	x	Am	Activity
I	C_2H_5–	1	$(C_2H_5)_2N$–	−
II	C_2H_5–	2	$(C_2H_5)_2N$–	++
III	C_2H_5–	3	$(C_2H_5)_2N$–	+
IV	C_2H_5–	1	$C_5H_{10}N$–	+
V	C_2H_5–	2	$C_5H_{10}N$–	+++
VI	C_2H_5–	3	$C_5H_{10}N$–	++
VII	C_6H_5–	2	$C_5H_{10}N$–	++++
VIII	C_6H_5–	3	$C_5H_{10}N$–	++

In Table II, thirteen new quaternary salts of previously reported β-amino alcohols are listed. In general, the formation of these quaternary salts from the amino alcohols proceeds slowly if the latter are dissolved in an excess of the alkyl halide, and the resulting solution is allowed to stand. The use of solvents such as nitromethane gave more rapid quaternization in certain cases Attempts to increase the rate of quaternization by heating were unsuccessful.

Pharmacological Activity

The general significance of the antispasmodic rating has been given in paper I[7] of this series, and details of the testing method have been recently reported by Cunningham and co-workers.[8] The quantitative significance of the rating scheme used throughout this series of papers has not as yet been reported. The rating of + indicates that no less than 1 mg. of the compound in 100 ml. of the testing bath gives a 50% relaxation of the spasm of a rabbit ileum made spastic with 0.1 mg. of Furmethide per 100 ml. bath. A rating of ++ indicates that the same effect is produced with no less than 0.1 mg. of the compound. Ratings of +++ and ++++ likewise vary successively by factors of ten in concentration.

Table I shows that the lower homologs, the α-amino alcohols, are less active than the higher homologs, the γ-amino alcohols, which, in turn, are less active than the β-amino alcohols. It is concluded therefore, that, in this type of com-

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(1) For paper IV in this series see THIS JOURNAL, **71**, 2054 (1949). Throughout this series of papers for generic names, we have preferred to use the term "alcohol" to mean the same as the term "carbinol." Thus, the amino alcohols retain the same prefix as the amino ketones from which they were usually derived.

(2) Denton, Neier and Lawson, *ibid.*, **71**, 2053 (1949).

(3) Denton, Lawson, Neier and Turner, *ibid.*, **71**, 2050 (1949).

(4) Henley and Turner, *J. Chem. Soc.*, 1182 (1931).

(5) Marxer, *Helv. Chim. Acta*, **24**, 209 (1941).

(6) Miescher and Marxer, United States Patent 2,411,664, November, 1946.

(7) Denton, Turner, Neier, Lawson and Schedl, THIS JOURNAL, **71**, 2048 (1949).

(8) Cunningham, *et al.*, *J. Pharmacol. Exptl. Therap.*, **96**, 151 (1949).