[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE UNIVERSITY, MANHATTAN, KANSAS]

Catalytic Decomposition of Carbonate Esters of 1,3-Diols[1,2]

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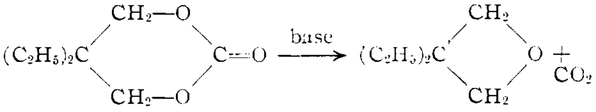
Carbonates of 2,2-dialkyl-1,3-diols, thermally stable by themselves, can be decomposed in good yield to 3,3-dialkyloxetanes and carbon dioxide by heating in the presence of a basic catalyst, such as potassium cyanide or potassium carbonate. Twenty bases of various types were investigated as catalysts. If there is a hydrogen atom on the carbon atom between the carbinol groups of the 1,3-diol, the carbonate ester decomposes principally to an allylic alcohol. Side reactions observed were cleavage to olefin, carbonyl compound and carbon dioxide, due to conjugate elimination, and to aldehyde and carbon dioxide, due to 1,3-hydride shift.

The thermal decomposition of carbonate esters of diols to form cyclic ethers and carbon dioxide has been described recently by several workers. The reaction is reported to apply to carbonate esters of 1,2-,[4] 1,3-,[5,6] 1,4-[6] and 1,5-diols,[6] but so far has been restricted to carbonates containing one or more free hydroxyl groups. Other carbonates reported either do not decompose at the usual temperatures employed or decompose in other ways.[6-8]

This potentially valuable synthesis of oxetanes thus has been restricted to preparation of oxetanes bearing one or two hydroxymethyl groups at position 3 on the ring. Since the marked effect of such hydroxyl groups may be due to internal catalysis,[9] it was thought that the presence of nucleophilic substances might catalyze the reaction with 1,3-carbonate esters not possessing hydroxymethyl groups.

Many inorganic bases were found to be catalysts for the decomposition of carbonate esters of 1,3-diols, though with varying effectiveness. The most extensive study was done on the decomposition of 5,5-diethyl-1,3-dioxan-2-one (I), the cyclic carbonate ester of 2,2-diethyl-1,3-propanediol, which yielded 3,3-diethyloxetane (II). Results with the best catalysts found are presented in Table I.[10]



I

II

The best catalyst found was solid potassium cyanide, by means of which a 65% yield of 3,3-diethyloxetane was obtained. The other catalysts represent a wide variety of types, and there seems to be no correlation between basicity and catalytic efficacy. They all seemed to operate in a heterogeneous manner, and no doubt several factors are important, including geometry of the surface, nucleophilic power of the anion and ability of the cation to coördinate with the oxygen atoms. Several bases were completely ineffective as catalysts under the conditions: calcium carbonate, guanidinium carbonate, sodium borate, powdered

TABLE I

PYROLYSIS OF 5,5-DIETHYL-1,3-DIOXAN-2-ONE

	Catalyst[a]	Reaction temp., °C.	Yield, % 3,3-diethyloxetane
1	KCN	235–250	65
2	Al_2O_3[b]	230–350	58
3	$CuCO_3 \cdot Cu(OH)_2$	180–220	55
4	NaCN	250–265	46
5	K_2CO_3	245–265	45
6	Na_2CO_3	255–260	39
7	Ag_2CO_3	240–260	37
8	CH_3CH_2COOK	240–250	39
9	CH_3COOK	240-250	24
10	$CH_3CO_2^- N(CH_3^+)_4$[c]	240–250	36
11	MgO	275-300	36
12	CaO	235-280	28
13	$NaOCH_3$	210–300	28[d]
14	KOH[e]	245-300	34[d]

[a] The amount used was 20% by weight of the dioxanone. [b] Activated alumina, basic. [c] This catalyst itself decomposed (to methylacetone and trimethylamine) simultaneously with the cyclic carbonate. [d] In addition, considerable, 2,2-diethyl-1,3-propanediol was formed by ester interchange or saponification. [e] Powdered.

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[1] Oxetanes X. Preceding paper in this series: S. Searles, R. G. Nickerson and W. K. Witsiepe, *J. Org. Chem.*, **24**, 1839 (1959).

[2] Supported in part by research grants from the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to these sponsors.

[3] Most of this material has been abstracted from the Ph.D. Thesis of Donald G. Hummel, Kansas State College, May, 1958.

[4] H. A. Bruson and T. W. Riener, THIS JOURNAL, **74**, 2100 (1952).

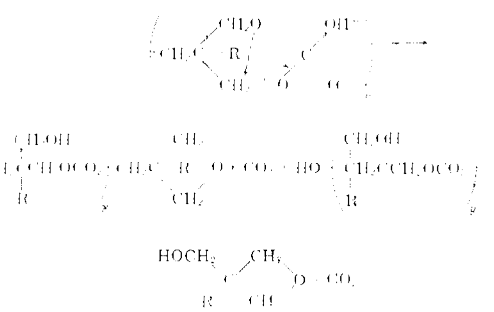
[5] W. Biedermann, K. Raichle and H. Schnell, German Patent Appl. F15046 (June 25, 1954).

[6] D. B. Pattison, THIS JOURNAL, **79**, 3455 (1957).

[7] J. L. R. Williams, K. R. Dunham and T. M. Leakso, *J. Org. Chem.*, **23**, 676 (1958).

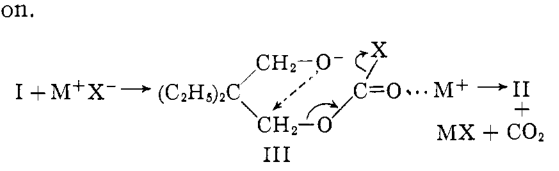
[8] W. H. Carothers and F. J. VanNatta, THIS JOURNAL, **52**, 314 (1930).

[9] It is believed that this is best explained by intermediate orthoester formation in the polymeric carbonate ester. The assumption of the previous workers that cyclic carbonate ester is a necessary intermediate appears to be unsupported and unnecessary.



[10] In contrast, heating 5,5-diethyl-1,3-dioxan-2-one with potassium thiocyanate gives rise to 3,3-diethylthietane, as reported by S. Searles and E. F. Lutz, THIS JOURNAL, **80**, 3168 (1958).

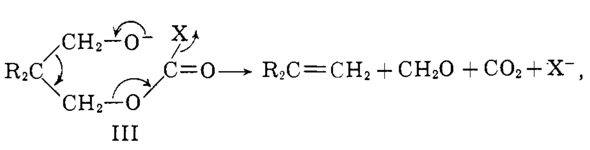
soft glass, triethanolamine and antipyrene. The results suggest that the catalyst functions by nucleophilic attack of the anion on the carbonyl carbon atom, with the resulting ester-alkoxide ion III undergoing an internal Williamson reaction.



This work was done with a cyclic carbonate ester because of its easy purification. In the earlier work the carbonate ester was not isolated,[5,6] although it was assumed that the cyclic form was the actual intermediate.[6] It seems reasonable, however, that a polymeric carbonate ester could react by the same mechanism; and indeed it was found here that poly-2,2-diethyl-1,3-propylene carbonate was converted into the oxetane II under the same conditions as used for the cyclic carbonate ester This may be due, of course, to the interconvertibility of cyclic and polymeric forms of the carbonate esters, which has been well established in the cases of trimethylene carbonate[8] and neopentylene carbonate,[11] under conditions similar to those used for oxetane formation.

The principal by-products from the reaction of 5,5-diethyl-1,3-dioxan-2-one appears to be formaldehyde and 2-ethyl-1-butene. These were identified by their physical properties, including infrared spectra, the dimedone derivative of the former and the dibromide of the latter.

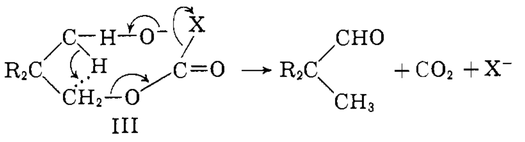
They probably arise from the alternative mode of decomposition of the alkoxide intermediate (III) by 1,4-elimination rather than from pyrolysis of



already formed 3,3-diethyloxetane. Pyrolysis of the oxetane ring in 3,3-dimethyloxetane and 3,3-diethyloxetane requires a temperature in excess of 450°.[12] This type of decomposition is very similar to the cleavage of 3-bromo-1-propanols with alkali.[1,13]

The pyrolysis of the carbonate esters of eight other 1,3-diols was also investigated with potassium carbonate as catalyst, as summarized in Table II. The pyrolyses of the carbonate esters of 2,2-dimethyl-1,3-propanediol and 3,3-dibenzyl-1,3-propanediol were analogous to that of the diethyl case described above and gave 2,2-dimethyloxetane and 2,2-dibenzyloxetane in good yields. This is a much better way of making these compounds, both with respect to convenience and yield, than the usual internal Williamson reaction on the 1,3-bromo alcohols.[1,13–15]

The formation of 3-ethyl-3-phenyloxetane, albeit in low yield, from the pyrolysis of the cyclic carbonate of 2-ethyl-2-phenyl-1,3-propanediol is of particular interest, as the reaction of the corresponding bromohydrin with alkali yields only formaldehyde and α-ethylstyrene.[1] The latter are formed also from the cyclic carbonate; the possible conjugation between the phenyl group and the olefinic linkage no doubt favors this mode of decomposition. The α-ethylstyrene was identified by oxidation to propiophenone. Another interesting product from this cyclic carbonate is 2-methyl-2-phenylbutanal, formed in 12.5% yield and identified through its semicarbazone. This may be considered to arise by a 1,3-hydride shift in the intermediate alkoxide III.



If the methylene carbon between the carbinol groups in a 1,3-diol is bonded to one or more hydrogen atoms, its carbonate ester may decarbonate to form an allylic alcohol rather than an oxetane. Carothers and VanNatta[8] observed this behavior with polymeric trimethylene carbonate heated to 210°, which decomposed to allyl alcohol. We have found that cyclic trimethylene carbonate decomposes in a like manner, but higher yield, with no oxetane detectable. This is similar to the pyrolysis of carbonate esters[7] (and other esters) of monohydric alcohols forming olefins, but the temperature required is much lower in the case of the 1,3-carbonates.

Pyrolysis of three other cyclic carbonates possessing one or two hydrogen atoms β- to both carbinyl oxygen atoms, likewise resulted principally in formation of corresponding allylic alcohols, as shown in Table II. In each case, the oxetane undoubtedly was formed also but was a minor product and could not be isolated in pure form on account of the small quantity and the high volatility. It was possible to concentrate the oxetane by distillation and to estimate crudely the amount from the infrared spectrum.[16] The cyclic carbonate of 2,2,4-trimethyl-1,3-pentanediol does not possess any hydrogen on C-2, but there is a hydrogen atom on C-4 which is β to one of the oxygen atoms. Pyrolysis of this compound gave chiefly the cyclic ether, but there was also formed some of the

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(11) S. Sarel and L. A. Pohoryles, THIS JOURNAL, **80**, 4596 (1958). These workers claimed that this property of reversible polymerization of cyclic 1,3-carbonate esters is lost when the carbon atom between the two carbinol groups in the diol is substituted by groups larger than methyl. No details about the carbonates of these ethyl- and higher-substituted 1,3-diols, however, were communicated, except for the statement that they were prepared by sodium alkoxide-catalyzed ester interchange with ethyl carbonate.

Our observations were that the products of this research with 2,2-dimethyl- and 2,2-diethyl-1,3-propanediol were in both cases polymers, which were broken down to the cyclic monomers on heating at 150–200°; this temperature was 50–100° higher than the head temperature, a simple distilling flask being used. In the diethyl case, a high polymer remained after this treatment, but further heating with potassium carbonate depolymerized it partially to cyclic carbonate. (This was actually very similar to the case of 2-methyl-2-*n*-propyl-1,3-propylene carbonate described by Sarel and Pohorlyes, which they implied to be different from the diethyl case.)

(12) P. E. Throckmorton, unpublished research.

(13) S. Searles and M. J. Gortatowski, THIS JOURNAL, **75**, 3030 (1953).

(14) G. M. Bennett and W. G. Philip, *J. Chem. Soc.*, 1938 (1928).

(15) R. Fonteyne and M. Ticket, *Natuurw. Tydschr.*, **25**, 29 (1943).

(16) G. M. Barrow and S. Searles, THIS JOURNAL, **75**, 1175 (1953).

unsaturated alcohol 2,2-dimethyl-3-pentene-1-ol. Thus, decomposition to unsaturated alcohol is much less favored when the hydrogen atom is β to only one oxygen atom. The small amount of 2-methyl-2-pentene also formed may arise from the 1,4-elimination process.

TABLE II

CATALYTIC PYROLYSIS OF OTHER 1,3-DIOXAN-2-ONES

Substituents	Temp., °C.	Products	Yield, %
None	210–240	Allyl alcohol	59
5,5-Dimethyl	230–240[a]	3,3-Dimethyloxetane	66
5,5-Dimethyl	245–265	3,3-Dimethyloxetane	45
5,5-Dibenzyl	200–210	3,3-Dibenzyloxetane	25
5-Ethyl-5-phenyl	200–210[a,b]	α-Ethylstyrene (+CH_2O)	20
		3-Ethyl-3-phenyloxetane	6
		2-Methyl-2-phenylbutanal	12
5-Methyl	205–240	3-Methyloxetane	2[c]
		2-Methylallyl alcohol	20
4-Methyl	190–195	2-Methyloxetane	15[c]
		Crotyl alcohol	71
4,4,6-Trimethyl	190–200	2,2,4-Trimethyloxetane	10[c]
		2-Methyl-2-penten-4-ol	64
4-Isopropyl-5,5-dimethyl	245–265[a]	2-Isopropyl-3,3-dimethyloxetane	49
		2,2,4-Trimethyl-3-pentene-1-ol	16
		2-Methyl-2-pentene	5

[a] Potassium cyanide was the catalyst in these experiments; in others potassium carbonate was the catalyst. [b] Pyrolysis carried *in vacuo* (40 mm.); the other experiments were all done at atmospheric pressure. [c] Estimated from the infrared spectrum of concentrated fractions.

The method described for pyrolysis of cyclic carbonates has been used in our laboratory for the preparation of other oxetanes, such as 2-oxaspiro-[3.3]heptane from the cyclic carbonate of 1,1-bis-(hydroxymethyl)-cyclobutane, and 2,6-dioxaspiro-[3.3]heptane from the polymeric carbonate of pentaerythritol.[17] These will be described separately, as they present additional features of interest.

Experimental[18]

1,3-Diols.—1,3-Propanediol, 1,3-butanediol, 2,2-dimethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol and 2-methyl-1,3-pentanediol were all obtained from the Eastman Kodak Co. 2,2-Dimethyl-1,3-pentanediol was furnished through the courtesy of the Tennessee Eastman Co. 2-Ethyl-2-phenyl-1,3-propanediol, 2,2-dibenzyl-1,3-propanediol and 2-methyl-1,3-propanediol were prepared by lithium aluminum hydride reduction of the corresponding malonic esters.[1,19,20] These compounds were purified by standard procedures until the physical properties agreed with those previously reported.

Cyclic Carbonates (1,3-Dioxan-2-ones).—The general procedure was to heat a mixture of 1.0 mole of the 1,3-diol and 1.1 moles of ethyl carbonate, containing 0.5 g. of previously dissolved sodium metal, at 130–170° with removal of ethyl alcohol by distillation. When approximately the theoretical amount of alcohol had been collected, the residue was taken up in an equal volume of benzene, washed with water, dried over calcium chloride and distilled, except the dibenzyl and ethylphenyl compounds. The solids were crystallized from ether or ligroin-benzene. Properties of the products obtained are summarized in Table III, except the cyclic carbonate from 2-methyl-1,3-propanediol which was prepared on too small a scale to permit efficient fractional distillation. (The crude product, which boiled at 121–125° (0.05 mm.), was about half starting diol, according to elemental analysis and infrared spectrum.) The cyclic carbonates all showed strong carbonyl absorption in the infrared at 5.6–5.7μ.

Catalytic Pyrolysis.—The general procedure is illustrated by the following example: A mixture of 10 g. of 5,5-diethyl-1,3-dioxan-2-one and 2 g. of potassium cyanide was heated in a 25-ml. 3-necked flask equipped with a thermometer, a gas inlet tube and a distillation head. When the temperature reached 235°, vigorous bubbling commenced, and a slow stream of nitrogen gas was introduced. The distillate was condensed in a receiver cooled in a Dry Ice-acetone-bath and connected to a calcium chloride tube. The odor of formaldehyde was evident at this exit of the receiver. The pyrolysis required about 45 minutes. The crude product, amounting to 6.8 g., was fractionally distilled over sodium metal to give 0.85 g. of olefinic material, b.p. 55–70°; 5.3 g. of material, b.p. 120–141°, the oxetane fraction; and 0.5 g. of starting dioxanone. Refractionation of the oxetane cut showed it to be 85% pure 3,3-diethyloxetane, b.p. 139–141°, n^{20}_D 1.4230 (reported[1] b.p. 138–140°, n^{20}_D 1.4230), corresponding to a yield of 65%.

Redistillation over sodium of the first fraction gave 0.3 g. of 2-ethyl-1-butene, b.p. 55–59°, n^{20}_D 1.3961 (reported[21] b.p. 64.68, n^{20}_D 1.39671). Its infrared spectrum was identical in all respects (except for the slightly greater intensity of a medium bond at 9.5 μ) with the published spectrum for 2-ethyl-1-butene.[22]

TABLE III

1,3-DIOXAN-2-ONES

Substituents	Yield, %	B.p. °C.	B.p. Mm.	M.p., °C. Obsd.	M.p., °C. Lit.
None	50	90–110	0.2	47–48	47–48[a]
4-Methyl[b]	60	100–110	.8		
5,5-Dimethyl	52	120–125	.2	115	110–111[c]
5,5-Diethyl	67	117–120	1.0[d]	44–45	45–46[c]
5-Ethyl-5-phenyl	74			99–100	99.5–100.5[c]
4,4,6-Trimethyl[e]	76	113–120	0.1	97.5–98	96–97
4-Isopropyl-5,5-dimethyl[f]	60	132	2[g]		
5,5-Dibenzyl[h]	73			227–229	

[a] Reference 8. [b] *Anal.* Calcd. for $C_5H_8O_3$: C, 51.72; H, 6.94. Found: C, 51.98; H, 7.01. [c] B. J. Ludwig and E. C. Piech, THIS JOURNAL, **73**, 5779 (1951). [d] Reference *c* reported b.p. 131–132° (2 mm.). [e] *Anal.* Calcd. for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 58.33; H, 8.29. [f] *Anal.* Calcd. for $C_9H_{16}O_3$: C, 62.76; H, 9.37. Found: C, 62.89; H, 9.29. [g] n^{20}_D 1.4580. [h] *Anal.* Calcd. for $C_{18}H_{18}O_3$: C, 76.56; H, 6.46. Found: C, 76.31; H, 6.69.

The presence of formaldehyde in the crude product was recognized by odor and by typical infrared absorption bands at 3.70 and 5.75μ. Treatment of a water extract of the crude product with dimedone reagent gave white crystals, m.p. 191–192°, undepressed by mixture with authentic dimedon derivative of formaldehyde (lit.[23] values 189°, 191°).

The yields of products from pyrolysis of 5,5-diethyl-1,3-dioxan-2-one with other catalysts are given in Table I. The products and yields thereof from other cyclic carbonates are summarized in Table II. The evidence for the structures assigned these products is presented in Table IV, with some additional evidence given at the end of this section. The infrared spectra of the products were taken in each case and agreed with the assigned structures.

In several cases where the products were predominantly allylic alcohols mixed with small amounts of oxetanes, a special procedure had to be used because of the difficulty of complete separation. Fractional distillation was carried out, concentrating the oxetane in the low boiling fractions, as evidenced by the presence of an absorption band in the infrared spectrum at about 10.3μ.[15] The remainder, or an aliquot thereof, was treated with α-naphthyl isocyanate. The α-naphthylurethan was recrystallized from ligroin to constant melting point and weighed. The yields of several

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[17] Unpublished research of P. E. Throckmorton and E. F. Lutz.

[18] Melting points and boiling points are uncorrected. Microanalyses were preformed by Weiler and Straus, Oxford, England, and by Micro-Tech Laboratories, Skokie, Ill.

[19] H. L. Yale, E. J. Pribyl, W. Braker, J. Bernstein and W. A. Lott, THIS JOURNAL, **72**, 3716 (1950).

[20] N. Rabjohn, T. R. Hopkins and R. C. Nagler, *ibid.*, **74**, 3215 (1952).

[21] F. D. Rossini, "Selected Values of Properties of Hydrocarbons," Am. Pet. Inst. Res. Proj. 44, Carnegie Inst. of Tech., Pittsburgh, Pa., Tables 8 a-E, pt. 2, and 8 k, pt. 2 (1957).

[22] "Catalog of Infrared Spectral Data," Am. Pet. Inst. Res. Proj. 44, Carnegie Inst. of Tech., Pittsburgh, Pa., Spectra No. 626, 711 and 712 (1947-1948).

[23] F. Wild, "Characterization of Organic Compounds," University Press, Cambridge, Eng., 1948, p. 138.

TABLE IV

IDENTIFICATION OF PRODUCTS

Compound	B.p., °C. (mm.) Obsd.	B.p., °C. (mm.) Lit.	n^{20}D Obsd.	n^{20}D Lit.	Derivative, m.p., °C.
3,3-Dimethyloxetane	80–81	78 (742)[a]	1.3950	1.3907[b]	
3,3-Diethyloxetane	139–141	138–140[b]	1.4230	1.4230[b]	
3-Ethyl-3-phenyloxetane[c]	215–225		1.5153		
2-Isopropyl-3,3-dimethyloxetane[d,e]	135		1.4157		
α-Ethylstyrene[a]	170–180	81–82 (20)[f]	1.5270		
2,4-Dimethyl-2-pentene	66–68	83.2[g]	1.3980	1.4040[g]	
Allyl alcohol	95–96	96–97[h]	1.4132	1.4134[h]	NU[i] 107.5–108[h]
2-Methylallyl alcohol	80–110	114.5[j]			NU[i] 78–79[k]
4-Methyl-3-pentene-2-ol	120–130	112[l]			NU[i] 82–84[m]
Crotyl alcohol	110–118	118 (764)[n]			NU[i] 88[n]
2,2,4-Trimethyl-3-penten-1-ol	163–166		1.4488		
2-Methyl-2-phenylbutanol	225–228	228–230	1.5195		S,[i] 152–152.5°
3,3-Dibenzyloxetane	135 (0.1)	135 (0.1)	1.5765[b]		

[a] G. M. Bennett and W. G. Philip, *J. Chem. Soc.*, 1938 (1928). [b] Reference 1. [c] *Anal.* Calcd. for $C_{11}H_{14}O$: C, 81.43; H, 8.70. Found: C, 79.72; H, 8.46. [d] Further details on identification in text of Experimental section. [e] *Anal.* Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.65; H, 12.52. [f] J. D. A. Johnson and G. A. R. Kon, *J. Chem. Soc.*, 2755 (1926). [g] F. D. Rossini, "Selected Values of Properties of Hydrocarbons and Related Compounds," Am. Pet. Inst. Res. Proj. 44, Carnegie Inst. Tech., Pittsburgh, Pa., Table 9a-E, pt. 2 (1954), which also gives d^{20}_4 0.6996; found for the material obtained here, d^{20}_4 0.689. [h] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941; this α-naphthylurethan is listed here with m.p. 108°. [i] NU = α-naphthylurethan, S = semicarbazone. [j] M. Tamele, C. J. Ott, K. E. Marple and G. Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941). [k] *Anal.* Calcd. for $C_{15}H_{15}O_2N$: N, 5.81. Found: N, 5.60. [l] E. P. Kohler, *Am. Chem. J.*, **38**, 556 (1907). [m] *Anal.* Calcd. for $C_{17}H_{19}O_2N$: N, 5.20. Found: N, 5.12. [n] K. Hess and W. Wustrow, *Ann.*, **437**, 256 (1924); the α-naphthylurethan is stated by these authors to melt at 89°. [o] J. Levy and A. Tabart, *Bull. soc. chim. France*, [2] **49**, 1785 (1931).

2-methylallyl alcohol, crotyl alcohol and 2-methyl-2-penten-4-ol reported in Table II were determined from the weights of pure urethans obtained in this manner.

Use of Polymeric Carbonate.—It was as satisfactory to use polymeric carbonate esters as cyclic esters for the oxetane synthesis, as shown by the following examples: (1) A mixture of 48.2 g. of polymeric 2,2-dimethyl-1,3-propanediol carbonate (an amorphous white powder, m.p. 71–91°, the crude undistilled transesterification product of the diol and diethyl carbonate) and 10.0 g. of anhydrous potassium carbonate was heated at 200–230°. The distillate was fractionally distilled to give 17.3 g. (54%) of 3,3-dimethyloxetane, b.p. 67–82°, n^{20}D 1.392–1.396. The pure oxetane obtained by distillation over sodium, b.p. 80.5–81°, n^{2}D 1.3950.

(2) Heating 79.0 g. of crude, polymeric 2,2-diethyl-1,3-propanediol carbonate (m.p. 60–64°) in the presence of 5.9 g. of potassium carbonate at 230–280° yielded 32.3 g. (57%) of 3,3-diethyloxetane, b.p. 130–142°, n^{20}D 1.416–1.423. The pure product was obtained by distillation over sodium, b.p. 140.5–141.0°, n^{20}D 1.4245.

Additional Structure Proofs.—The structure of the hydrocarbon from 5-ethyl-5-phenyl-1,3-dioxan-2-one was proved to be α-ethylstyrene by oxidizing 0.1 g. of it with 0.35 g. of potassium permanganate in 1 ml. of glacial acetic acid. After the reaction mixture was shaken at room temperature a few minutes and warmed briefly on the steam-cone, it was diluted with water, neutralized and extracted with ether. To the oil remaining after evaporation of the ether was added 2,4-dinitrophenylhydrazine reagent, and the derivative was isolated in the usual way. The m.p., 191–192°, was identical to that of authentic propiophenone DNP, kindly supplied by Dr. G. Dana Johnson, and the mixed m.p. showed no depression.

The structure of 2-isopropyl-3,3-dimethyloxetane (from 4-isopropyl-5,5-dimethyl-1,3-dioxan-2-one) was proved by lithium aluminum hydride reduction. A solution of 1.2 g. of it, 0.2 g. of lithium aluminum hydride and 20 g. of tetrahydrofuran was refluxed for 35 hours and then decomposed with 3 ml. of 20% sodium carbonate. After filtration and distillation of the solvent, 0.45 g. of an oil remained which distilled at 145–148° at atmospheric pressure, with n^{20}D 1.4270, giving a 3,5-dinitrobenzoate melting at 99–100°. The expected alcohol, 2,4-dimethyl-2-hexanol, is reported[24] to have a b.p. of 145°, n^{20}D 1.4280, m.p. of 3,5-dinitrobenzoate 101–102°.

For the allylic alcohol from 4,4,6-trimethyl-1,3-dioxan-2-one, the structure 4-methyl-3-penten-2-ol was assigned rather than that of its allylic isomer, on the basis of the infrared and n. m. r. spectra. The details of the assignment will be presented in a separate paper on the preferred steric source of pyrolysis to form allylic alcohols.[25]

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[24] F. S. Bridson-Jones, G. D. Buckley, L. H. Cross and A. P. Driver, *J. Chem. Soc.*, 2999 (1951).

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