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Cyclic Ethers Made by Pyrolysis of Carbonate Esters

BY DEXTER B. PATTISON

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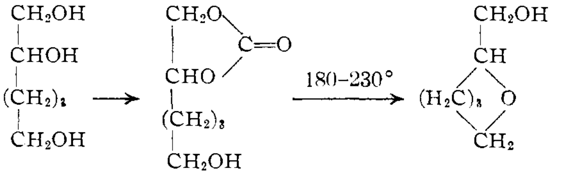
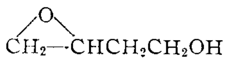
Cyclic ethers containing three to six atoms in the ring are readily prepared in good yield by pyrolysis of the corresponding carbonate esters, if an activating hydroxyl group is present.

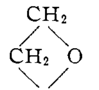
Cyclic ethers containing three, four, five or six atoms in the ring are prepared by pyrolysis of cyclic carbonate esters having one or two hydroxyl groups. The reaction is more general than has been demonstrated previously. H. Bruson[1] reported that glyceryl carbonate on pyrolysis gives glycidol, which contains a three-membered epoxide ring. Near the completion of the present work, a German patent application[2] was published describing the preparation of 3-ethyl and 3-methyloxetane-3-methanol by pyrolysis of the carbonate esters of trimethylolpropane and trimethylolethane, respectively. In the German work, phosgene was used to make the carbonate ester of trimethylolpropane. In our work a safer and more convenient laboratory method was employed for making the carbonate esters, namely, ester interchange with diethyl carbonate or ethylene carbonate.

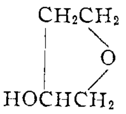
A typical example of the formation of a six-membered oxide ring is the preparation of tetrahydropyran-2-methanol in 62% yield from 1,2,6-hexanetriol *via* the cyclic carbonate ester. In this case the 1,5-epoxide was formed, and there was none of the 1,2- or the 1,6-epoxide. The structure was proved by the infrared spectrum which was identical with that of an authentic sample of tetrahydropyran-2-methanol.



A typical example of the formation of a five-membered ring is the synthesis of 3-hydroxytetrahydrofuran in 88% yield from 1,2,4-butanetriol *via* the cyclic carbonate ester. In this case the three possible structures of the product are shown below.


1,2-epoxide


1,3-epoxide


1,4-epoxide

It was shown that the product was not a 1,2-epoxide because the material did not react at 100° with *n*-butylamine; and under these conditions glycidol, a 1,2-epoxide, is converted quantitatively to high boiling products, mainly 3-butylamino-1,2-propanediol. The compound had the same boiling point, refractive index and infrared spectrum as an authentic sample of 3-hydroxytetrahydrofuran[3] prepared by dehydration of 1,2,4-butanetriol using sulfuric acid as catalyst.

Four-membered oxide ring compounds which have been synthesized by this method are 3-ethyl-oxetanemethanol, 3-methyl-3-oxetanemethanol and 3,3-oxetanedimethanol.[4] They were made in yields of 87, 77 and 34%, respectively, from trimethylolpropane, trimethylolethane and pentaerythritol.

Cyclic carbonates containing no hydroxyl groups are much more stable than carbonate ester containing a hydroxyl group. For example a mixture of 2,2-diethylpropanediol and its cyclic carbonate ester can be distilled at 220° under slightly reduced pressure without decomposition, whereas the cyclic carbonate of trimethylolpropane decomposes rapidly at 180–200° to carbon dioxide and 3-ethyl-3-oxetanemethanol.

TABLE I

PREPARATION OF EPOXIDES BY PYROLYSIS OF CARBONATE ESTERS

Starting triol or tetrol	Alkyl carbonate	Product % Yield[a]	Product Conversion[a]
1,2,6-Hexanetriol	Ethylene	62	78
1,2,4-Butanetriol	Diethyl	88	82
Trimethylolpropane	Ethylene	72	69
Trimethylolpropane	Diethyl	87	92
Trimethylolpropane	Dibutyl	83	93
Trimethylolethane	Diethyl	77	97
Pentaerythritol	Diethyl	34	100

[a] $$\%\ \text{Yield} = \frac{\text{g. product} \times \dfrac{\text{mol. wt. polyol}}{\text{mol. wt. product}}}{\text{g. polyol charged} - \text{g. polyol recovered}} \times 100$$

$$\%\ \text{Conversion} = \frac{\text{g. polyol charged} - \text{g. polyol recovered}}{\text{g. polyol charged}} \times 100$$

Experimental

Typical preparations employing ethylene carbonate or diethyl carbonate are described below. In Table I yield data are given, and in Table II physical properties and analytical data are recorded.

Tetrahydropyran-2-methanol from 1,2,6-Hexanetriol.—A mixture of 670 g. of 1,2,6-hexanetriol (5.0 moles) and 493 g. of ethylene carbonate (5.5 moles) was kept at 140–150°, and ethylene glycol (336 g.) was removed by distillation at 26–10 mm. pressure. The pot temperature was raised gradually to 250° and the pressure fell, due to carbon dioxide evolution.

Under full motor pump vacuum 510 g. of product was obtained. Part of this boiled at 100–130° under 30–130 mm. pressure, but near the end, when carbon dioxide evolution had ceased, the boiling point was 150–175° and the pressure was 2–10 mm. Redistillation through an efficient column gave 281 g. of tetrahydropyran-2-methanol, boiling at 57° at 4 mm. or 78° at 13 mm. and 150 g. of 1,2,6-hexanetriol, boiling at 174–180° at 6 mm.

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(1) H. Bruson and R. Riener, THIS JOURNAL, **74**, 2100 (1952).

(2) German Application F 15046 (Jan. 5, 1956), W. Biedermann to Bayer.

(3) W. Reppe, *et al.*, *Ann.*, **596**, 80 (1956).

(4) F. Govaert and M. Beyaert, *C. A.*, **34**, 5415² (1940); *Proc. Acad. Sci., Amsterdam*, **42**, 790 (1939).

TABLE II

PROPERTIES OF EPOXIDES CONTAINING HYDROXYL GROUPS

Compound	B.p., °C.	Press., mm.	$n^{25}D$	Carbon, % Calcd.	Carbon, % Found	Hydrogen % Calcd.	Hydrogen % Found	Hydroxyl No. Calcd.	Hydroxyl No. Found
Tetrahydropyran-2-methanol	57	4.2	1.4561	62.1	62.2	10.2	10.2	484	486
					62.1		10.6		487
							10.2		
3-Hydroxytetrahydrofuran	110	5.6	1.4493	54.6	54.6	9.1	9.0	638	629
					54.8		9.3		632
					54.9		9.3		
3-Ethyl-3-oxetanemethanol	84	2.8	1.4517	62.1	62.0	10.4	10.2	484	486
					62.4		10.4		483
3-Methyl-3-oxetanemethanol	80	4.0	1.4449	58.8	58.6	9.8	9.9		
					58.8		9.9	549	543
									546
3,3-Oxetanedimethanol	155	3.5	(Solid)	50.9	50.4	8.5	8.7	951	907
					50.5		8.8		906

3-Ethyl-3-oxetanemethanol from Trimethylolpropane.—A mixture of 268 g. of trimethylolpropane (2.0 moles), 236 g. of diethyl carbonate (2.0 moles) and 0.10 g. of potassium hydroxide dissolved in 5 ml. of absolute alcohol was refluxed until pot temperature was below 105° (15 minutes), and the mixture was distilled keeping the head temperature 76–78°. Distillation was continued until the pot temperature was 145°, and then the pressure was reduced gradually to 50 mm., maintaining the pot temperature at 140–150°. The weight of distillate was 179 g. (theory 184 g. alcohol). Upon heating above 180°, carbon dioxide evolution was rapid and most of the material distilled at 190–210° pot temperature, 90–140° head temperature and 50-90 mm. pressure. Near the end the pressure became 2–10 mm. and the head temperature rose. Redistillation through an efficient column gave: 13.4 g., b.p. 84–86° at 3.5 mm.; 136.6 g., b.p. 84–84.5 at 2.8 mm.; 24.4 g., b.p. 84.5-85.5 at 2.8 mm.; 26.1 g., residue.

The main fraction was analytically pure 3-ethyl-3-oxetanemethanol, and from the residue analytically pure trimethylolpropane was obtained by distillation.

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[CONTRIBUTION FROM THE AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Endocyclic α,β-Unsaturated Ketones. VI.[1] Ultraviolet and Infrared Absorption Spectra and Resonance Stabilizations

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New data are presented for the ultraviolet absorption spectra of thirteen ketones. These compounds are members of three series, *viz.*, 1,1-dimethyl-2-keto-1,2-dihydronaphthalene (1,1-dimethyl-2(1*H*)-naphthalenone) (II), 4,4-dimethyl-1-keto-1,4-dihydronaphthalene (4,4-dimethyl-1-(4*H*)-naphthalenone) (I), and perinaphthenone-7 (1-(1*H*)-benzonaphthenone) (III). With previously reported data for eight related compounds, the spectra are discussed with respect to resonance stabilizations, effect of nature and position of substituents, and type of conjugation. New infrared spectral data are presented for twenty-one ketones in the three series. These results are discussed with respect to the same factors.

Ultraviolet Absorption Spectra Studies

Introduction.—Studies of ultraviolet absorption spectra of α,β-unsaturated ketones have mainly dealt with open chain systems, with some treatment of endocyclic series. The effect of conjugation of the unsaturated ketone system with phenyl groups has been studied, and chromophores assigned to ultraviolet absorption bands.[4,5] Absorption in the 2300–2500 Å. region was ascribed to the benzoyl or acrylophenone chromophore, and intense absorption from 2800 to 3500 Å. to the cinnamoyl chromophore. The effect of linear and crossed conjugation, and of endo- and exocyclic double bonds on the spectra of α,β-unsaturated ketones has been discussed.[6]

It was observed[4,7,8] that various substituents on the α- or β-carbon atom of the α,β-unsaturated ketone system have a bathochromic effect on the ultraviolet absorption bands. The extent of the shift varied with the nature of the substituent, and the position of attachment. Resonance forms were suggested for the chromophores responsible for the characteristic bands.[4] The importance of chelation in the β-hydroxy[7] and β-amino ketones was discussed.[4] Since such chelation or ionic interaction is impossible in the endocyclic series, it seemed of considerable interest to study these endocyclic compounds.

The compounds used in these studies are all of

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[1] For paper No. V, see, N. H. Cromwell and R. D. Campbell, *J. Org. Chem.*, **22**, in press (1957).

[2] Du Pont Teaching Fellow, 1954–1955. Ph.D. Thesis, University of Nebraska, 1956.

[3] To whom inquiries regarding this article should be addressed.

[4] N. H. Cromwell and W. R. Watson, *J. Org. Chem.*, **14**, 411 (1949).

[5] W. B. Black and R. E. Lutz, THIS JOURNAL, **77**, 5134 (1955).

[6] H. S. French and L. Wiley, *ibid.*, **71**, 3702 (1949); H. S. French, *ibid.*, **74**, 514 (1952).

[7] K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946).

[8] A. L. Nussbaum, O. Mancera, R. Daniels, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **73**, 3263 (1951).