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New Addition Reactions. I. Reaction of Epoxides with Ketene

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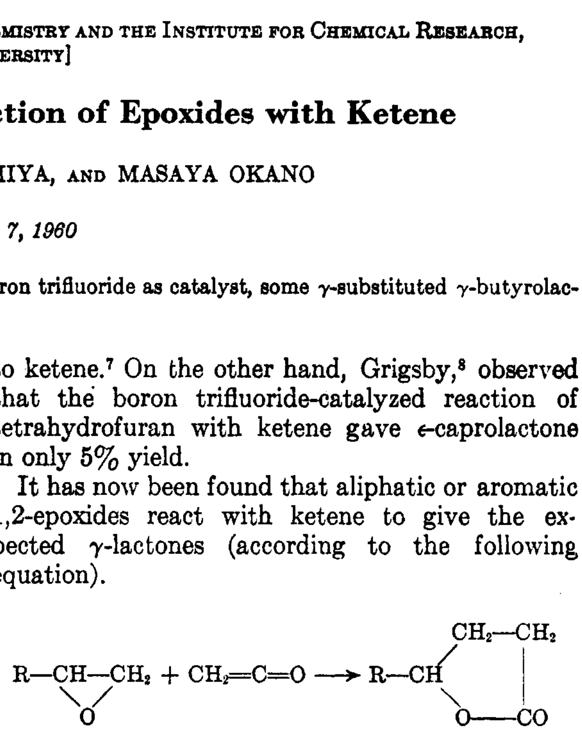
By the addition reaction of 1,2-epoxides with ketene, using boron trifluoride as catalyst, some γ-substituted γ-butyrolactones have been obtained in about 10% yield based on epoxide.

One of the authors has been surveying some organic reactions involving the "crosswise condensation" of two components.[1] To make a survey of addition reactions between two polar unsaturated bonds, we have listed various groups such as epoxy, carbonyl, nitrile, azomethine, isocyanate, nitroso and ylene (phosphinemethylene and phosphineimide) as shown in Table I.[2] On studying some unknown combinations in the Table, we found some new addition reactions. This paper is concerned with the formation of γ-lactones from epoxides and ketene.

Some information on the formation of lactones by addition reactions is known. In the noncatalyzed reaction of benzoquinone with ketene, the formation of a β-lactone was first observed by Staudinger *et al.*[3] Later, Küng,[4] Steadman,[5] and Hagemeyer *et al.*[6] reported that in the presence of Lewis acid catalysts β-lactones were prepared in good yields by the addition of aliphatic aldehydes or ketones to ketene.[7] On the other hand, Grigsby,[8] observed that the boron trifluoride-catalyzed reaction of tetrahydrofuran with ketene gave ε-caprolactone in only 5% yield.

It has now been found that aliphatic or aromatic 1,2-epoxides react with ketene to give the expected γ-lactones (according to the following equation).



When the ketene gas was passed into an ether solution of epoxides the with 5 mole % (based on epoxide) boron trifluoride etherate at *ca.* 10° for an hour and a half, lactones were obtained in about 10% yield. In the case of stannic chloride catalyst, a smaller amount of product was formed. Although it is known that a quaternary ammonium halide such as tetraethylammonium bromide is highly effective in the addition of epoxide to isocyanate,[9] it is ineffective in this reaction and only dehydroacetic acid was obtained. Variations in catalyst concentration, reaction time, and temperature have little effect on the yield of product. These results are shown in Table II.

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(1)(a) R. Oda, *Some Organic Reactions* (in Japanese), Kyoritsu, Tokyo, Japan, 1950, pp. 33, 95, and 130. (b) R. Oda, *Mem. Fac. Eng. Kyoto Univ.*, **14**, 195 (1952). (c) R. Oda *et al.*, *Chemistry of High Polymers, Japan*, **16**, 137 (1959).

(2) C. K. Ingold and H. A. Piggott [*J. Chem. Soc.*, 2793 (1922)] had mentioned briefly the possibility of such an addition reaction.

(3) H. Staudinger *et al.*, *Ber.*, **41**, 1355 (1908); *Ann.*, **380**, 243 (1911).

(4) F. E. Küng, U. S. Patent **2,356,459**; *Chem. Abstr.*, **39**, 88 (1945).

(5) T. R. Steadman, U. S. Patent **2,424,589**; *Chem. Abstr.*, **41**, 7413 (1947).

(6) H. J. Hagemeyer, Jr., *et al.*, *Ind. Eng. Chem.*, **41**, 765 (1949); U. S. Patent **2,462,357**; *Chem. Abstr.*, **43**, 3840 (1949).

(7) Some different type catalysts appeared in the patent literature. *Cf.* H. E. Zaugg, *Org. Reactions*, VIII, 337 (1954).

(8) W. E. Grigsby, U. S. Patent **2,443,351**; *Chem. Abstr.*, **42**, 7324 (1948).

(9) G. P. Speranza and W. J. Pepper, *J. Org. Chem.*, **23**, 1922 (1958).

TABLE I

SURVEY OF ADDITION REACTIONS BETWEEN UNSATURATED BONDS

	$\underset{\diagdown\;O\;\diagup}{-CH-CH_2}$	>C=O	>C=N—	—C≡N	—N=C=O	>C=C=O	—N=O	⩾P=C< ⩾P=N—
$\underset{\diagdown\;O\;\diagup}{-CH-CH_2}$	1[a]							
>C=O	2[b]	9[e]						
>C=N—	3	10	16[j]					
—C≡N	4	11	17	22[o]				
—N=C=O	5[c]	12[f]	18[k]	23	27[p]			
>C=C=O	6	13[g]	19[l]	24	28[q]	31[t]		
—N=O	7	14[h]	20[m]	25	29[r]	32[u]	34	
⩾P=C< (PM)								
⩾P=N— (PI)	8[d]	15[i]	21[n]	26	30[s]	33[v]	35[w]	36

Products and references: [a] Linear polyether (*e.g.*, Polyox). [b] Dioxolane (cyclic acetal and ketal). (i) M. T. Bogert and R. O. Roblin, Jr., *J. Am. Chem. Soc.*, **55,** 3741 (1933). (ii) G. Willfang, *et al.*, *Ber.*, **70,** 2167 (1937); **74,** 145 (1941). (iii) A. A. Petrov, *J. Gen. Chem. U. S. S. R.*, **10,** 981 (1940) [*Chem. Abstr.*, **35,** 3603 (1941)]. Similarly, epoxide reacts with carboxylic ester to give alkoxydioxolane [H. Meerwein, *Angew. Chem.*, **67,** 379 (1955)], and ethyleneimine reacts with aldehyde or ketone to give oxazolidine [J. B. Doughty, C. L. Lazzell, and A. R. Collett, *J. Am. Chem. Soc.*, **72,** 2866 (1950)]. Oxazolidine [J. B. Doughty, C. L. Lazzell, and A. R. Collett, *J. Am. Chem. Soc.*, **72,** 2866 (1950)]. [c] 2-Oxazolidinone. (i) K. Gulbins and K. Hamann, *Angew. Chem.*, **70,** 705 (1958). (ii) Ref. 9. [d] Cyclopropane (from PM) (derivative). D. B. Denny and M. J. Boskin, *J. Am. Chem. Soc.*, **81,** 6330 (1959). [e] Cyclic trimer (*e.g.*, trioxymethylene, paraldehyde). Linear polyether (*e.g.*, Derlin). [f] Schiff base. (i) H. Staudinger and R. Endle, *Ber.*, **50,** 1042 (1917). (ii) T. Lieser and G. Nischk, *Ann.*, **569,** 73 (1950). [g] β-Lactone or olefine. Ref. 7, p. 313. [h] Nitroso compound does not react with ketone, but gives Schiff base with thioketone [A. Schöring and K. H. Browski, *Chem. Ber.*, **92,** 2602 (1959)]. [i] Olefin (from PM). (i) G. Wittig, *Angew. Chem.*, **68,** 505 (1956). (ii) U. Schöllkoph, *ibid.*, **71,** 260 (1959). PI does not react with aldehyde [H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2,** 644 (1919)]. See also the reaction of PM with carboxylic ester [G. Wittig, *Chem. Ber.*, **87,** 1318 (1954)]. [j] Cyclic dimer or trimer. (i) Ref. 2. (ii) M. M. Sprung, *Chem. Revs.*, **26,** 311 (1940). [k] 2-Diazetidinone. A. Senier and F. G. Shepheard, *J. Chem. Soc.*, **95,** 504 (1909). [l] β-Lactam. (i) J. C. Sheehan and E. J. Corey, *Org. Reactions*, **9,** 395 (1957). (ii) H. Krässig and H. Ringsdorf, *Makromol. Chem.*, **22,** 167 (1957). (iii) A. M. v. Leusen and J. F. Arens, *Rec. trav. chim.*, **78,** 551 (1959). [m] Oxadiazetidinone. C. K. Ingold, *J. Chem. Soc.*, **125,** 87 (1924). [n] Unchanged [H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2,** 643, 644 (1919)]. [o] Cyclic trimer. (i) A. Lottermoser, *J. prakt. Chem.*, [2], **54,** 132 (1896). (ii) A. Cook and D. Jones, *J. Chem. Soc.*, 278 (1941). (iii) J. J. Ritter and R. D. Anderson, *J. Org. Chem.*, **24,** 208 (1959). [p] Cyclic dimer or trimer. (i) J. H. Saunders and R. J. Slocombe, *Chem. Revs.*, **43,** 221 (1948). (ii) R. G. Arnold, J. A. Nelson, and J. J. Verblanc, *Chem. Revs.*, **57,** 54 (1957). Linear polyamide (1-nylon). V. E. Shashoua, *et al.*, *J. Am. Chem. Soc.*, **81,** 3156 (1959); **82,** 866 (1960). [q] Malonimide. H. Staudinger, O. Göhring, and M. Schöller, *Ber.*, **47,** 40 (1914). [r] Azo compound. Footnote f—(i), (ii). [s] Ketenimine (from PM) and carbodimide (from PI). (i) H. Staudinger and J. Meyer, *Helv. Chim. Acta,* **2,** 635 (1919). (ii) H. Staudinger and J. Meyer, *Ber.*, **53,** 72 (1920). [t] Cyclic dimer (*e.g.*, diketene). Linear polyketone. (Derivative). (i) P. R. Johnson, H. M. Barnes, and S. M. McElvain, *J. Am. Chem. Soc.*, **62,** 964 (1940). (ii) J. Lal, *J. Polymer Sci.*, **41,** 399 (1959). [u] 3-Oxazetidinone or Schiff base. H. Staudinger and S. Jelagin, *Ber.*, **44,** 365 (1911). [v] Allene (from PM). G. Lüscher, dissertation Eidgen. Techn. Hochschule, Zürich (1922) [*cf.* J. Meyer, *Chem. Ber.*, **89,** 842 (1956)]. Ketenimine (from PI). Footnotes—(ii). [w] Schiff base. Footnote h.

TABLE II

FORMATION OF γ-LACTONES FROM EPOXIDES AND KETENE

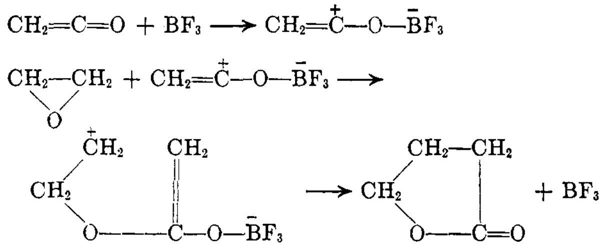
			Reaction Condition			
Epoxide	Solvent	Catalyst,[a] Mole %	Temp.	Time, hr.	Product	Yield,[a] %
Ethylene oxide	Ether	BF_3 etherate, 5	5	1.5	γ-Butyrolactone	5
Propylene oxide	Ether	BF_3 etherate, 5	9	1.5	γ-Valerolactone	9
"	Ether	BF_3 etherate, 10	9	1.5	γ-Valerolactone	8
"	Ether	BF_3 etherate, 20	9	1.5	γ-Valerolactone	11
"	Ether	BF_3 etherate, 5	12	3.0	γ-Valerolactone	13
"	Ether	None	9	1.5	γ-Valerolactone	Trace
Epichlorohydrin	Ether	BF_3 etherate, 5	9	1.5	γ-Chloromethyl-γ-butyrolactone	10
"	Benzene	BF_3 etherate, 5	50	1.5	γ-Chloromethyl-γ-butyrolactone	14
"	Benzene	None	50	1.5	γ-Chloromethyl-γ-butyrolactone	Trace
"	Carbontetrachloride	$SnCl_4$, 5	10	1.5	γ-Chloromethyl-γ-butyrolactone	3
"	Benzene	$(C_2H_5)_4NBr$, 5	15	1.5	Dehydroacetic acid (m.p. 107°)[b]	3
Styrene oxide	Ether	BF_3 etherate, 5	9	1.5	γ-Phenyl-γ-butyrolactone	9

[a] Based on epoxide. [b] Not depressed on admixture with an authentic sample prepared by the procedure of T. Isozima, *J. Chem. Soc. Japan, Ind. Chem. Section*, **37,** 773 (1954).

In the reaction with substituted ethylene oxides, two structures of the product are possible. However, all melting or boiling points of the lactones from these epoxides agreed with the data of γ-substituted γ-butyrolactones in the literature. In addition, the identity of the propylene oxide-ketene adduct with γ-valerolactone was established by a mixed melting point determination as its phenylhydrazides. Thus it is obvious that the ring-opening of epoxides occurs between the α-carbon and oxygen atom as shown in the above equation.

The yields in this reaction are usually low. This may be due to the reaction rate or to the equilibrium, but it is not possible to decide from our data which is responsible. Moreover, a possibility of the loss of epoxide by competitive polymerization during the reaction and by simultaneous evaporation of the low boiling epoxide on distillation of solvent may be considered. Although the maximum yields in the addition of epichlorohydrin to ketene is only 14%, the conversion percentage amounts to 60% based on consumed epichlorohydrin.

On the basis of the acid-catalyzed reaction, a probable mechanism is suggested.



EXPERIMENTAL[10]

Generation of ketene. Ketene was prepared by the pyrolysis of diketene according to the procedure of Boese.[11]

As an example of the procedure used for the addition reaction, the following is an illustration. In all cases, about 0.5 mole of epoxide was treated with about 3.5 moles of ketone in 300 ml. of solvent.

γ-Butyrolactone. In a 500-ml. flask fitted with a inlet tube, a thermometer, and a glass coil surrounded by ice and salt which was connected with a calcium chloride tube, were placed 300 ml. of dry ether and 4.0 g. (0.028 mole) of boron trifluoride etherate. The mixture was cooled in an ice salt bath to 0°, and 25 g. (0.57 mole) of ethylene oxide was gradually added to it. Then, the ketene (*ca.* 3.5 moles) was led slowly into the above solution at a rate of *ca.* 100 g./hr. for 1.5 hr. The temperature was maintained below 10 during the reaction. After removal of the solvent, the lactone was distilled at 55–57° (3 mm.). lit.[12] 89° (12 mm.), yielding 2.5 g. (5%).

This product was further characterized as the phenylhydrazide of the γ-hydroxy acid, m.p. 78°, which showed no melting point depression with an authentic sample.

Anal. Calcd. for $C_{10}H_{14}N_2O_2$; C, 61.83; H, 7.27; N, 14.42. Found: C, 61.80; H, 7.18; N, 14.66.

γ-Valerolactone. In a similar way, ketene was treated with propylene oxide to give γ-valerolactone, b.p. 60–61° (2 mm.), lit.[13] b.p. 78° (4 mm.). The phenylhydrazide melted at 76° (lit.[14] b.p. 76–79°) and also showed no depression when mixed with an authentic sample. In the reaction with epichlorohydrin or styrene oxide, the reaction mixture was poured into water after completion of the reaction, and neutralized with aqueous potassium carbonate. The ether was removed by evaporation and the residue was distilled *in vacuo* or recrystallized. γ-Chloromethyl-γ-butyrolactone from epichlorohydrin boiled at 120–123° (9 mm.) [lit.[15] b.p. 132–135° (12 mm.)]. Saponification gave the acid with neutral equivalent 147 (calcd. for γ-hydroxy acid $C_5H_9ClO_3$, 152.6). γ-Phenyl-γ-butyrolactone from styrene oxide melted at 38° (lit.[16] m.p. 37°), and it afforded the oxy acid, m.p. 74° (lit.[16] m.p. 75°) and neutral equivalent 181 (calcd. 180.2).

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[10] Melting and boiling points are uncorrected.

[11] A. B. Boese, Jr., *Ind. Eng. Chem.*, **32**, 16 (1940).

[12] S. S. G. Sircar, *J. Chem. Soc.*, 901 (1928).

[13] H. A. Schuette and P. P. T. Sah, *J. Am. Chem. Soc.*, **48**, 3165 (1926).

[14] W. Wisliceus, *Ber.*, **20**, 402 (1887).

[15] H. Leuchs and O. Splettstosser, *Ber.*, **40**, 304 (1907).

[16] R. Fittig and H. W. Jayne, *Ann.*, **216**, 103, 106 (1883).