Synthesis and Epoxidation of Bis(2-cyclopentenyl) Carbonates

JOHN W. LYNN, ALEX E. BRODHAG[1] and SAMUEL W. TINSLEY
Research and Development Dept., Union Carbide Chemicals Co., South Charleston, W. Va.

BIS(2-CYCLOPENTENY) CARBONATE, previously unreported, was prepared by three different methods: ester-exchange between 2-cyclopentenol and diethyl carbonate, phosgenation of potassium 2-cyclopentenylate, and reaction of sodium carbonate with 2-cyclopentenyl chloride (*3, 4*). The pure carbonate was observed to undergo rapid decomposition to CO_2, 2-cyclopentenol, and cyclopentadiene at about 100° C. Epoxidation was effected by treatment with peracetic acid in ethyl acetate (*1*) to yield a new diepoxy carbonate, bis(2,3-epoxycyclopentyl) carbonate. Similar compounds have been reported previously (*2*).

LITERATURE CITED

(1) Frostick, F.C., Phillips, B., Stacher, P.S., *J. Am. Chem. Soc.* **81**, 3350 (1959).
(2) Heiberger, C.A. (to Ohio-Apex Co.), British Patent **666,560**, 1952.
(3) Kukui, K., Yoneda, S., Takayama, H., Ketano, H., *Kugyo Kagaku Zasshe*, **63**, 2146 (1960).
(4) Mueller, A.C., Shohad, E.C., (to Shell Development Co.), U. S. Patent **2,795,572** (1959).

Table I. Synthesis and Epoxidation of Bis(2-cyclopentenyl) Carbonates

Compound	Formula	B.B. °/mm.[a]	%, Calcd. C	%, Calcd. H	%, Found C	%, Found H
Bis(2-cyclopentenyl) carbonate	$C_{11}H_{14}O_3$	80/0.5	68.02	7.27	67.81	7.40
Bis(2,3-epoxycyclopentyl) carbonate	$C_{11}H_{14}O_5$	121/0.09	58.40	6.24	58.61	6.21

[a] All temperatures are uncorrected.

---

[1] Present address, Chemical Abstracts Service, Ohio State University, Columbus 10, Ohio.

RECEIVED for review March 4, 1963. Accepted March 22, 1963.

Polyol Esters of 3-Butenoic Acid

JOHN W. LYNN and RICHARD L. ROBERTS
Research and Development Dept., Union Carbide Chemicals Co., South Charleston, W. Va.

SEVERAL GLYCOL and triol esters of 3-butenoic acid were prepared as intermediates to epoxy resins and for evaluation as reactive plasticizers for vinyl chloride resins. To date, only mono-lower alkyl esters of this acid have been reported.

The esters were prepared by direct esterification of 3-butenoic acid (Method A) in the absence of catalyst and also by transesterification of ethyl 3-butenoate using a titanium tetralkylate catalyst. The use of an acidic catalyst (Method B) caused partial isomerization of the 3-butenoate system to be conjugated crotonate system. Physical properties for the several polyol esters of 3-butenoic acid are tabulated and method of preparation are given in Table I.

Table I. Polyol Esters of 3-Butenoic Acid: $(CH_2=CHCH_2CO_2)_xR$

R	Method	B.P.,[a] °C.	Mm.	n_D^{30}	d_{20}^{20}	Purity[b] %	Yield	%, Calcd. C	%, Calcd. H	%, Found, C	%, Found, H
$-CH_2CH_2-$	A	97	2	1.4469	1.0532	99.5	90	60.59	7.12	60.65	6.88
$-CH_2\acute{C}HCH_3$	B	90	1.5	1.4422	1.0237	99.4	86	62.25	7.6	62.22	8.0
$-CH_2CH(C_2H_5)\acute{C}HC_3H_7$	B	129	1.5	1.4483	0.9744	99.7	92	68.05	9.28	68.46	9.15
$-CH_2\acute{C}H(CH_2)_3CH_2-$	B	Residue		1.4645	1.0642	97.3	93	63.8	7.74	63.2	7.62
$CH_3CH_2C(CH_2-)_3$	A	170	1.5	1.4634	1.0598	...	77.4	63.9	7.70	64.02	7.58

[a] All boiling points are uncorrected. [b] Based on saponification.

RECEIVED for review March 13, 1963. Accepted March 22, 1963.