Bicyclic Diepoxides

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NEW BICYCLIC diepoxide monomers were synthesized in the search for thermally stable transparent expoxide resins.

EXPERIMENTAL

Preparation of bis[2-(bicyclo[2.2.1]hept-5-ene)-methyl] carbonate and bis [2-(bycyclo[2.2.1]heptane-5,6-expoy)-methyl] carbonate. Transesterification of bicyclo[2.2.1] hept-5-ene-2-methanol and diethyl carbonate was accomplished at 155° C. using a small piece of sodium as the catalyst. Sixty-two per cent of the theoretical amount of ethyl alcohol was obtained. This compound was expoxidized using perbenzoic acid in benzene at 5° C. The yield was 22 per cent.

Preparation of bicyclo[2.2.1]hept-5-ene-2-methyl, bicylo-[2.2.1] hept-5-ene-2 carboxylate and 5,6-expoxybicyclo[2.2.1]-heptane-2-methyl-5+,6+-epoxybicyclo[2.2.1]heptane-2-carboxylate. The unepoxidized compound was obtained by two synthetic methods, one, the Tischenko reaction of bicyclo-[2.2.1]hept-5-ene-2-carboxaldehyde and the other, esterification of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid and bicyclo[2.2.1]hept-5-ene-2 methanol. Seventy per cent yield was obtained with latter procedure. This compound was epoxidized with perbenzoic acid in benzene at 5° C.

Preparation of bis[2-(bicyclo[2.2.1]hept-5-ene)-methyl] oxide and bis[2-(bicyclo[2.2.1]heptane-5,6-epoxy)-methyl] oxide. The unepoxidized compound was synthesized by the Williamson method from the potassium alcoholate of bicyclo[2.2.1]hept-5-ene-2-methanol and bicyclo[2.2.1]hept-5-ene-2-methyl chloride at 195° C. Another synthetic route was by the reaction of 5-methylene bicyclo[2.2.1]hept-2-ene and a mixture of sodium salt of bicyclo[2.2.1]hept-5-ene-2-methanol and bicyclo[2.2.1]hept-5-ene-2-methanol. All of the expected endo-exo isomers were identified by NMR. None of the isomers were obtained in a pure state. The ether was epoxidized using perbenzoic acid in benzene.

Preparation of bicyclo[2.2.2]oct-5-ene-2-methyl, bicyclo-[2.2.2]oct-5-ene-2-carboxylate and 5,6-epoxybicyclo[2.2.2]-octane-2-methyl-5',6'-epoxybicyclo[2.2.2]octane -2- carboxylate. The Tischenko reaction of bicylco-[2.2.2]oct-2-ene-5-carboxyldehyde was used to prepare the unepoxidized compound. Perbenzoic acid in benzene was used to prepare the epoxide. The epoxide was purified by crystallization.

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Table I. Properties of Compounds Prepared

Compound	B.P., ° C.	M.P., ° C.	N_D^{24}	d_{24}	Analysis
Bis[2-(bicyclo[2.2.1]hept-5-ene)-methyl]carbonate	140 at 1 mm. Hg		1.5031	...	For $C_{17}H_{22}O_3$: Calcd: C, 74.45; H, 8.03 Found: C, 73.98; H, 7.87
Bis[2-(bicyclo[2.2.1]heptane-5,6-epoxy)-methyl]carbonate	170 at 0.08 mm. Hg		1.5108	1.2288	For $C_{17}H_{22}O_5$: Calcd. C, 66.48; H, 7.20 Found: C, 66.40; H, 7.28
Bicyclo[2.2.1]hept-5-ene-2-methyl, bicyclo[2.2.1]hept-5-ene-2-carboxylate	117 at 0.2 mm. Hg		1.5071	1.0704	For $C_{16}H_{20}$: Calcd. C, 78.77; H, 8.15 Found: C, 78.72; H, 8.09
5,6-Epoxybicyclo[2.2.1]heptane-2-methyl-5',6'-epoxybicyclo-[2.2.1]heptane-2-carboxylate	135–6 at 0.07 mm. Hg	125–6			For $C_{16}H_{20}O_4$: Calcd. C, 69.56; H, 7.24 Found: C, 70.73; H, 7.25
Bis-[2-(bicyclo[2.2.1]hept-5-ene)-methyl]oxide	95–98 at 0.2 mm. Hg[a] 98–103[b]	45–9	1.5071	1.010	For $C_{16}H_{22}O$: Calcd. C, 83.5; H, 9.58 Found: C, 83.8; H, 9.62[a] Found: C, 83.3; H, 9.52[b]
Bis(5,6-epoxybicyclo[2.2.1]heptane-2-methyl)carbonate (from solid ether)[b]	124 at 0.05 mm. Hg	75–78 121–124			For $C_{10}H_{22}O_3$: Calcd. C, 73.3; H, 8.45 Found: C, 72.6; H, 8.23
Bicyclo[2.2.2]oct-5-ene-2-methyl, bicyclo[2.2.2]oct-5-ene-2-carboxylate	151 at 0.2 mm. Hg	105–6			For $C_{18}H_{24}O_2$: Calcd. C, 79.41, H, 8.85 Found: C, 78.90; H, 8.65
5,6-Epoxybicyclo[2.2.2]octane-2-methyl-5',6'-epoxybicyclo-[2.2.2]octane-2-carboxylate		195–196			For $C_{18}H_{24}O_4$: Calcd. C, 71.05; H, 7.89 Found: C. 70.39; H, 8.05

[a] Liquid isomer at room temperature.
[b] Solid isomer at room temperature.