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A CONVENIENT PREPARATION OF (—)-β-3,4-EPOXYCARANE

W. Cocker and D.H. Grayson

University Chemical Laboratory, Trinity College, Dublin 2.

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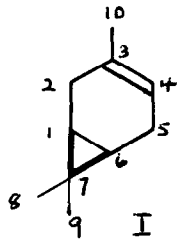
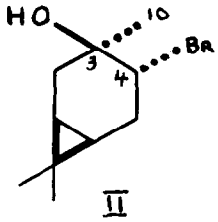
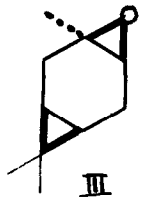
(+)-Car-3-ene (I) rapidly reacts with N- bromosuccinimide in aqueous dioxan or in t- butanol containing calcium carbonate to give a high yield of (—)-4α-bromo-trans-caran-3β-ol (II), which on treatment with potassium t- butoxide in t- butanol gives (—)-β-3,4-epoxycarane (III) in 55% overall yield from car-3-ene. This is a more convenient route to the epoxide than that starting from (+)-α-3,4-epoxycarane.[1]



I



II



III

Dry powdered calcium carbonate (2 g., 2 x 10^{-2} mole), water (10 c.c.), purified[2] dioxan (20 c.c.), and N- bromosuccinimide (7 g., 4 x 10^{-2} mole) were added in this order to (+)-car-3-ene (2.7 g., 2 x 10^{-2} mole), $[\alpha]_D^{20}$ + 15.4° (c 5.0 in EtOH), and the mixture was stirred for 2 hr., the temperature rising initially to 50°. The mixture was poured into water (50 c.c.), filtered, the solid residue was washed with ether, and the filtrate extracted with ether (2 x 100 c.c.). The combined extract, washed first with water (3 x 100 c.c.), then with sodium thiosulphate (5%; 20 c.c.), and evaporated, gave a pale brown oil (4 g., 87%), which rapidly solidified. It was crystallised from hexane giving the bromohydrin (II), m.p. 50-52° (decomp.), $[\alpha]_D^{20}$ —55° (c 2.0 in CCl_4), ν_{max} 3268, 2890, 1456, 1370, 1319, 1280, 1245, 1192, 1130, 1112, 1082, 996, 968, 951, 924, 883, 824, 804, 763, and 714 cm^{-1}, τ (CCl_4), 6.01 (m, H4), 7.92 (s, OH, exchanged with D_2O), 8.70 (s, 3H, H10), 8.98 and 9.01 (s, 6H, H8, H9).

The bromohydrin is unstable on exposure to air and on distillation at atmospheric

pressure it affords a mixture of m- and p- cymene in the ratio (g.l.c.) of 40:60.

Potassium t- butoxide (0.5 g.) in t- butanol (5 c.c.) was added to a solution of the bromohydrin (0.5 g.) in t- butanol (10 c.c.), the mixture was set aside for 2 hr., and then poured into water (50 c.c.). It was extracted with ether (3 x 20 c.c.) and the extract washed thoroughly with water, giving an oil (0.28 g.) which after chromatography on silica gel afforded (±)-β-3,4-epoxycarane (III) (0.25 g., 81%), $[\alpha]_D^{20} -5^\circ$ (c 2.0 in EtOH) identical in g.l.c., i.r. and n.m.r. with a sample prepared by the alternative method.[1]

REFERENCES

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