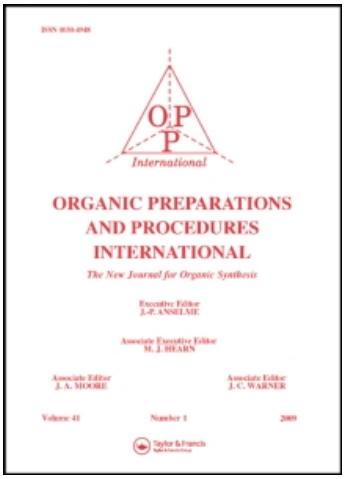

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1,5-DIBROMO- 3-*tert*-BUTYLPENTANE

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1,5-DIBROMO-3-tert-BUTYLPENTANE

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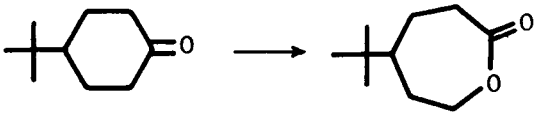
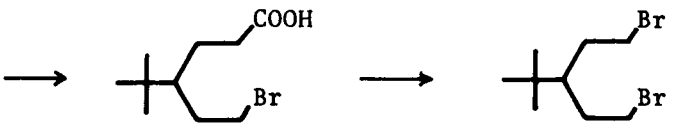
The title compound, 1,5-dibromo-3-tert-butylpentane (I), is a valuable intermediate to a possible conformationaly stable 4-tert-butylcyclohexane analogue. For example, in connection with the study of 4-tert-butyl-1-silacyclohexane derivatives,[1] I was required in quantity. Previously reported[2] synthesis of I starting from 4-tert-butylpyridine appeared rather inconvenient to us. Accordingly, we prepared I by the following three-step synthesis from commercially available 4-tert-butylcyclohexanone.[3]



(II) (III)



(VI) (I)

EXPERIMENTAL

Preparation of 5-tert-butyl-2-oxepanone (III).- To a solution of 0.219 mole of perbenzoic acid in 380 ml of dichloromethane was added 31 g (0.201 mole) of 4-tert-butylcyclohexanone. The mixture was stirred at room temperature overnight, washed three times with dil. aqueous $NaHCO_3$, aqueous sodium sulfate and water, then dried over sodium sulfate. Fractional distillation gave 8 g of recovered 4-tert-butylcyclohexanone and 25.5 g (0.149 mole, 100% yield) of 5-tert-butyl-2-oxepanone, bp. 100-105° (4 mm); mp. 51-54°; nmr (CCl_4, δ): 0.90 (s, tert-Bu), 2.54 (t, J=4.2Hz, CH_2CO), 4.15 (t, J=3.6Hz, CH_2-O); ir (KBr, cm^{-1}): 2940 (ν_{C-H}), 1723 ($\nu_{C=O}$), 1195, 1180 (ν_{C-O}).

Preparation of 5-bromo-3-tert-butylhexanoic acid (IV).- A mixture of 20 g (0.168 mole) of potassium bromide and 300 ml of 48% hydrobromic acid was placed in a 500 ml three-necked flask and cooled to -30° in a Dry Ice-methanol bath. Then 60 ml of conc. H_2SO_4 was added slowly. To this mixture was added 55 g (0.323 mole) of III. The resulting solution was stirred at room temperature for 2 h, and then on a steam bath for 10 h. The mixture was diluted with an equal volume of water after cooling, saturated with ammonium sulfate then extracted with ether. Distillation gave 67 g (0.267 mole, 83% yield) of IV, bp. 133-143° (4 mm) as a light yellow viscous oil, n_D^{20} 1.4860; nmr (CCl_4, δ): 0.95 (s, tert-Bu), 2.28 (t, J=8.4Hz, CH_2COO),

3.32 (t, J=7.8Hz, CH_2Br); ir (neat, cm^{-1}): ∿3000 (ν_{O-H}), 1713 ($\nu_{C=O}$), 565 (ν_{C-Br}).

Anal. Calcd. for $C_{10}H_{19}Br$: C, 47.82; H, 7.62%. Found: C, 48.11; H, 7.77%.

Preparation of 1,5-dibromo-3-tert-butylpentane (I).- In a 300 ml three-necked flask equipped with a sealed stirrer, a pressure-equalizing dropping funnel and a reflux condenser whose top was connected to a calcium chloride tube, was placed 30 g (0.139 mole) of red mercuric oxide. The flask was then heated with a hot-blower under reduced pressure to dry the mercuric oxide. The calcium chloride tube was then replaced with a mercury seal and 60 ml of freshly distilled carbon tetrachloride was added in an atmosphere of nitrogen. A solution of 35 g (0.22 mole) of bromine and 50 g (0.199 mole) of IV in 50 ml of carbon tetrachloride was then added with vigorous stirring over a period of 1 h. The mixture was stirred for an additional 1 h at 60°, filtered with suction and the filtrate steam-distilled. The lower portion of the steam distillate was separated and the upper portion was extracted with carbon tetrachloride. The combined solution was dried over calcium chloride. After the solvent was removed, fractional distillation gave 34.5 g (0.121 mole, 61% yield) of I as a colorless oil, bp. 98-99° (3 mm), lit.[2] 87-88° (0.7 mm).

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3. The required 4-tert-butylcyclohexanone may be prepared from 4-tert-butylphenol by reduction with W-7 Raney nickel followed by chromic acid oxidation.[4]
4. K. Schemering, J. Amer. Chem. Soc., 69, 1121 (1947).

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