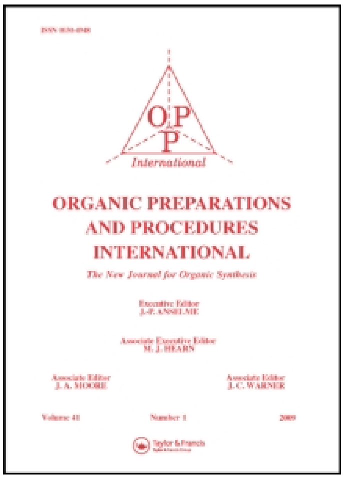

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DEHALOGENATION OF 7,7-BIS(BROMOMETHYL) BICYCLO[4.1.0]HEPT-3-ENE

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DEHALOGENATION OF 7,7-BIS(BROMOMETHYL) BICYCLO[4.1.0]HEPT-3-ENE

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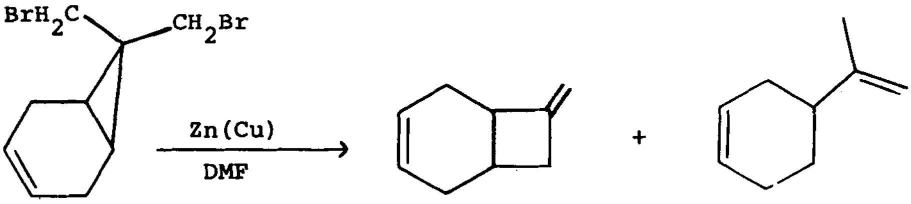

I II III

The rearrangements of cyclopropylcarbinyl systems have been studied at some length.[1,2] In the absence of specific attempts to quench carbonium ion formation,[2] dehalogenations of bis-bromomethylcyclopropanes take place with extensive rearrangement. This fact has been utilized in the dehalogenation of dibromide I which proceeds with rearrangement to afford 7-methylenebicyclo[4.2.0]oct-3-ene (II) in addition to 4-isopropenyl-cyclohexene (III).

EXPERIMENTAL

7,7-Bis(hydroxymethyl)bicyclo[4.1.0]hept-3-ene. To a slurry of 13.5 g (0.36 mole) of lithium aluminum hydride in 500 ml of ether was added 26.5 g (0.11 mole) of 7,7-dicarbethoxybicyclo-[4.1.0]hept-3-ene[3] dropwise. The mixture was refluxed overnight, cooled, and hydrolyzed by the careful addition of 36 ml of water. The solid was filtered and washed with four 50 ml portions of 1:10 methanol-ether. Evaporation of the combined filtrates gave an oil which crystallized on standing. Recrystallization from methylene chloride afforded 13.8 g (85%) of diol, mp 87-89°; $\nu_{max}^{CH_2Cl_2}$ 3600 and 3375 cm^{-1}.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.90; H, 9.19.

7,7-Bis(tosyloxymethyl)bicyclo[4.1.0]hept-3-ene. A solution of 8.9 g (0.06 mole) of diol in 40 ml of triethylamine and 20 ml of methylene chloride was cooled to 0° and 30 g (0.16 mole) of p-toluenesulphonyl chloride added. The mixture was stirred at 0° overnight, 25 ml of water followed by 25 ml of 10% sulfuric acid was added and the mixture stirred at 0° for one hour. The aqueous layer was extracted with three 25 ml portions of methylene chloride and the combined organic layers washed with three 10 ml portions of 10% sulfuric acid and 50 ml of water. The solution was dried over potassium carbonate, filtered, and evaporated. Recrystallization of the residue from carbon tetrachloride gave 17.2 g (62%) of ditosylate, mp 97-99°; $\nu_{max}^{CHCl_3}$ 3015, 1365, and 1175 cm^{-1}.

Anal. Calcd. for $C_{23}H_{26}O_6S_2$: C, 59.72; H, 5.67. Found: C, 59.79; H, 5.73.

7,7-Bis(bromomethyl)bicyclo[4.1.0]hept-3-ene. To a solution of 6.3 g (0.013 mole) of ditosylate in 60 ml of acetone was added a solution of 4.0 g (0.046 mole) of lithium bromide in 50 ml of acetone. The mixture was stirred at room temperature overnight, treated with 300 ml of water and extracted with four 50 ml portions of ether. Removal of solvent gave an oil which was recrystallized from pentane at -60° to afford 3.2 g (75%) of I, mp 40-41°; $\nu_{max}^{CCl_4}$ 3020, 2895, 2830 and 1435 cm^{-1}; nmr(CCl_4)τ 8.68 (s, 2, cyclopropyl), 7.64 (s, 4, =CH-<u>CH</u>$_2$-), 6.45 (s, 2, <u>endo</u>-CH_2Br), 6.29 (s, 2, <u>exo</u>-CH_2Br) and 4.32 (s, 2, -CH=CH-).

<u>Anal</u>. Calcd. for $C_9H_{12}Br_2$: C, 38.32; H, 4.25. Found: C, 38.53; H, 4.20.

<u>Dehalogenation</u>. To a cooled (0°) stirred slurry of Zn(Cu),[4,5] in 13 ml of dry DMF was added a solution of 1.0 g (0.0036 mole) of I in 5 ml of dry DMF. The mixture was stirred at 0° for three hours, filtered, and the filtrate treated with 200 ml of water. The aqueous solution was extracted with four 40 ml portions of pentane, and solvent removed by distillation through a 40 cm Vigreux column. The residue was subjected to preparative glpc on a 3' x 0.25" column packed with 20% XE-60 ON 60/80 Diatoport (Column A) at 45°. The glpc trace essentially consisted of two peaks. The longer retention time (46 min) peak (132 mg, 30%) was identified as 7-methylenebicyclo[4.2.0]oct-3-ene, ν_{max}^{neat} 3075, 3040, 2845, 2915, 1670, 1430 and 875 cm^{-1}; nmr(CCl_4)τ 8.17-6.67 (broad absorption, 8), 5.32 (s, 2, =CH_2) and 4.17 (s, 2, -CH=CH-).

<u>Anal</u>. Calcd. for C_9H_{12}: C, 89.93; H, 10.07. Found: C, 89.65; H, 9.89.

The shorter retention time peak (75 mg, 17%) was identified as 4-isopropenyl cyclohexene,[6] ν_{max}^{neat} 3080, 3030, 2900, 1645, 886 and 719 cm^{-1}; nmr(CCl_4)τ 8.17 (s, 3, CH_3-), 7.8-8.25 (7, allylic and methylene), 5.32 (s, 2, =CH_2), 4.33

(s, 2, -CH=CH-).

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.20; H, 11.30.

7,7-dimethylbicyclo[4.1.0]hept-3-ene (IV). Reduction of 7,7-bis(toxyloxymethyl)bicyclo[4.1.0]hept-3-ene, 2.97 g (0.0064 mole) with 0.46 g (0.012 mole) of lithium aluminum hydride was accomplished in the usual manner (vide supra). Solvent was removed from the ethereal filtrate by distillation and the residue subjected to preparative glpc (Column A, 45°) affording 0.56 g (72%) of a liquid (retention time = 32 min) identified as IV, ν_{max}^{neat} 3025, 2905, 1660 and 985 cm^{-1}; nmr (CCl_4)τ 9.39 (m, 2, cyclopropyl), 9.19 (s, 3, endo-CH_3), 8.97 (s, 3, exo-CH_3), 8.15-7.67 (m, 4, -CH_2-), and 4.50 (s, 2, =CH).

Anal. Calcd. for C_9H_{12}: C, 89.93; H, 10.07. Found: C, 89.65; H, 9.94.

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4. Prepared from 10.5 g of zinc by the method described by E. LeGoff, J. Org. Chem., 29, 2048(1964)

5. The Zn(Cu) must be carefully washed with ether to remove all traces of acetic acid. Failure to do this results in the formation of a third product, 7,7-dimethylbicyclo-[4.1.0]hept-3-ene. This material may be conveniently prepared by lithium aluminum hydride reduction of the corresponding ditosylate.

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