

A Demonstration of Chirality in an Alkylidenecyclobutane Derivative

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ALKYLIDENECYCLOALKANE COMPOUNDS of the general structure (I) are chiral about an axis.¹ The first demonstration of chirality in such a system, where $n = 2$, was the resolution of 4-methylcyclohexylideneacetic acid.² We now report a demonstration of chirality in a system where $n = 1$.

2,2,4,4-Tetramethyl-3-tetrahydropyranoxycyclobutanone (II)³ was converted into the 3-ethylidene-2,2,4,4-tetramethylcyclobutanol derivative (III) by ethylenetriphenylphosphorane in ether. As difficulty was experienced in purifying the compound, it was converted by methanolysis in the presence of hydrochloric acid into the alcohol (IV), which was purified by distillation (b.p. 82°/20 mm.); m.p. 50–51°, n.m.r.† (CCl₄) δ 5.06 (q, 1H, J 6.5 c./sec.), 3.52 (s, 1H), 2.00 (s, 1H, concn. dependent), 1.57 (d, 3H, J 6.5 c./sec.), and 1.11 p.p.m. (4 s, 12H, Figure A). This compound conforms to the structure (I; $n = 1$) and should therefore exist in enantiomeric forms. Introduction of an asymmetric carbon atom during the formation of derivatives of this alcohol should give rise to a mixture of diastereoisomers which, in principle, should be distinguishable by physical methods. The tetrahydropyranoxo-derivative has an asymmetric carbon atom and therefore the pure alcohol (IV) was reconverted into this derivative (III) by treatment with dihydropyran and a catalytic amount of toluene-*p*-sulphonic acid; n.m.r.† (CCl₄) δ 5.04 (q, 1H, J 6.5 c./sec.), 4.45 (m, 1H), 3.55 (s and br m, 3H), 1.55 (d, J 6.5 c./sec. and br m, 8.6H), 1.12 p.p.m. (seven lines, 12.4 H, Figure B). The n.m.r. spectrum shows that a mixture of diastereoisomers has been produced in an almost 1:1 mixture. The region of the saturated methyl groups contains four singlets of equal intensity in the spectrum of the alcohol (IV) (Figure A) but in the spectrum of the derivative (III), this region contains seven lines, one of which is broadened and is due to two lines of almost identical chemical shift (Figure B). Thus there are eight lines, confirming the presence of diastereoisomers.‡

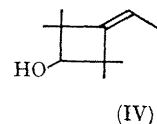
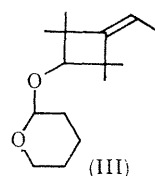
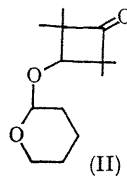
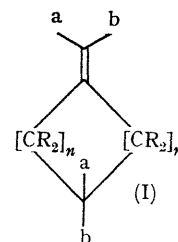
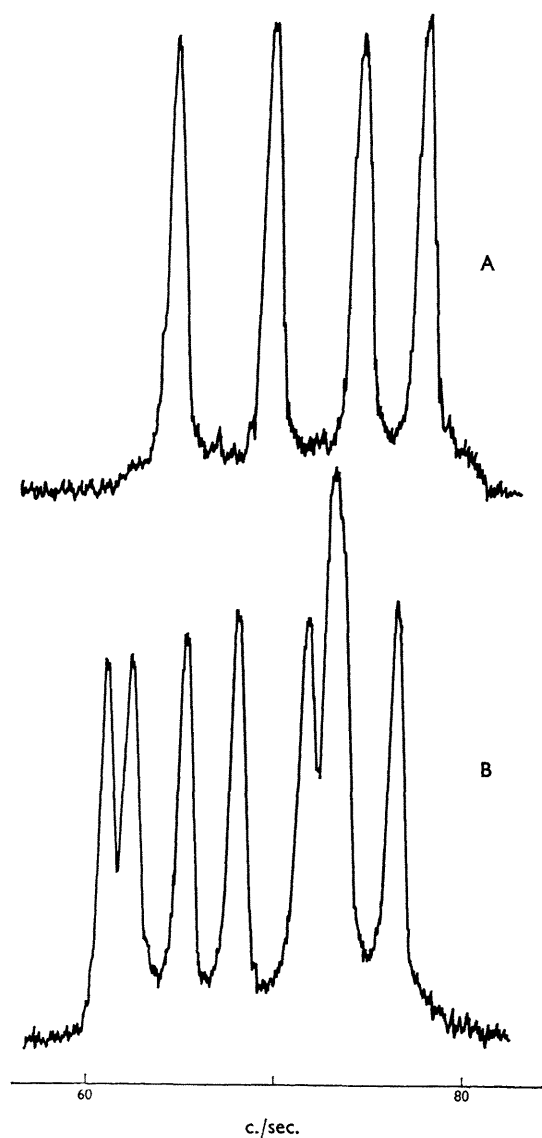


FIGURE. Absorptions of saturated methyl groups in the n.m.r. spectra of compounds (III) and (IV) at 60 Mc./sec.

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† δ (in p.p.m.) relative to internal SiMe₄.

‡ Each of these diastereoisomers occurs as a racemic modification.

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² W. H. Perkin, W. J. Pope, and O. Wallach, *Annalen*, 1909, 371, 180; *J. Chem. Soc.*, 1909, 95, 1789.

³ C. F. Burrige and D. P. G. Hamon, *Chem. Comm.*, 1968, 206.