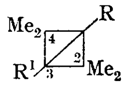
Methyl 2,2,2,4-Tetramethylbicyclo[1,1,0]butane-1-carboxylate

By MISS C. BURRIDGE and D. P. G. HAMON*

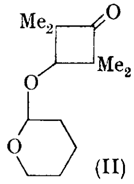
(*Department of Organic Chemistry, The University of Adelaide, Adelaide, S.A., Australia,* 5000)

WIBERG *et al.*[1] have suggested that the bicyclo-[1,1,0]butane system is probably the most highly strained of the two-ring carbocyclic systems. Evidence[2] suggests an interplanar angle of about 121°. If this is the case then two of the substituents, one at C-2 and one at C-4 take up a pseudo 1,3-diaxial relationship to one another. Groups with larger steric requirements than hydrogen should therefore decrease the stability of such molecules and it was of interest to know if compounds such as (I) could be prepared. Recent publications[3] have described the syntheses of two compounds (Ia and Ib). This Communication describes the synthesis of (Ic) by a simple intramolecular cyclisation of the type used for the synthesis of sterically less-crowded bicyclobutanes,[4] and shows that this route can be extended to 2,2,4,4-tetramethyl homologues.

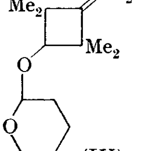
Tetrahydropyranyloxy-2,2,4,4-tetramethylcyclobutan-1-one (II) was converted, in 94% yield, into the 3-methylene-2,2,4,4-tetramethylcyclobutanol derivative (III), [i.r. 3050, 1670 cm.$^{-1}$, δ (CCl_4)† 4·65 (singlet 2H), $>C=CH_2$], by methylenetriphenylphosphorane in ether.[6] Hydroboration followed by oxidation with alkaline hydrogen peroxide gave in 82% yield a mixture of the two isomeric alcohols (IV).‡ Oxidation of these primary alcohols by chromic acid in acetone followed by extraction with sodium hydroxide§ and subsequent acidification yielded (50%) the hydroxy-acids (V)‡ (m.p. 100—128°) esterified by



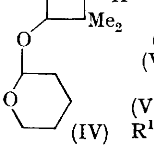
(I) (a) $R=R^1=CO_2Me$
(b) $R=R^1=Cl$
(c) $R=CO_2Me$,
$R^1=H$



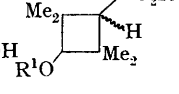
(II)



(III)



(IV)



(V) $R=R^1=H$
(VI) $R=Me$
$R^1=H$
(VII) $R=Me$,
$R^1=SO_2\cdot C_6H_4\cdot Me\text{-}p$

---

† δ in p.p.m. from Me_4Si as internal standard.

‡ I.r., n.m.r., and analytical data confirm the structure and isomeric nature of this mixture.

§ Not soluble in sodium hydrogen carbonate solution possibly due to steric hindrance to solvation of the anion.

diazomethane in almost quantitative yield into the esters (VI).‡ The toluene-*p*-sulphonate derivatives (VII)‡ (m.p. 60—84°) of these alcohols were heated with sodium hydride in 1,2-dimethoxyethane at 50° for 48 hr. to yield, after filtration and evaporation of the solvent, an oil which was essentially pure (Ic).¶ The structure of (Ic) was substantiated by the following spectral observations: *m/e* 168 $[M^+]$, n.m.r.† $\delta = \mathbf{3\cdot61}$ (3H singlet), 2·03 in (1H singlet)[7] 1·25 and 1·30 (two peaks of equal intensity, total of 12H), i.r. 3050 cm.$^{-1}$ stretch of hydrogen on small ring, 1710 cm.$^{-1}$ ester carbonyl.[8]

(*Received, November 6th*, 1967; *Com.* 1200.)

¶ Traces of 1,2-dimethoxyethane ($\delta = 3\cdot45$, $3\cdot31$) and mineral oil ($\delta \simeq 1\cdot2$) were the only peaks not assignable, in the n.m.r. to (Ic).

[1] K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, 1965, **21**, 2749.

[2] M. D. Harmony and K. Cox, *J. Amer. Chem. Soc.*, 1966, **88**, 5049.

[3] M. F. Neumann, *Angew. Chem. Internat. Edn.*, 1967, **6**, 79; E. J. Corey and M. Jautelat, *J. Amer. Chem. Soc.*, 1967, **89**, 3912; M. R. Rifi, *ibid.*, p. 4442.

[4] E. P. Blanchard, jun., and A. Cairncross, *J. Amer. Chem. Soc.*, 1966, **88**, 487, and references therein.

[5] R. H. Hasek, E. V. Elam, J. C. Martin, and R. G. Nations, *J. Org. Chem.*, 1961, **26**, 700.

[6] R. E. Ireland and L. N. Mander, *J. Org. Chem.*, 1966, **31**, 2540.

[7] In ethoxycarbonylbicyclo[1,1,0]butane the ring juncture hydrogen occurs at $\delta = 1\cdot97$ p.p.m. (K.B. Wiberg and R. P. Ciula, *J. Amer. Chem. Soc.*, 1959, **81**, 5261).

[8] Possibly at longer wavelength due to conjugation with the bicyclobutane ring [compound (VII) — C=O, 1735 cm.$^{-1}$], M. Pomerantz and E. W. Abrahamson, *J. Amer. Chem. Soc.*, 1966, **88**, 3970, and references therein.