2,2,5,5-Tetramethylbicyclo[4,1,0]hept-1(6)-en-7-one

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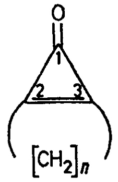
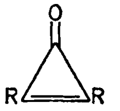
Summary The title compound, the most strained in the alicyclic ring-fused cyclopropenone series, has been synthesised; its physical and chemical properties reflect the large strain energy in the system.

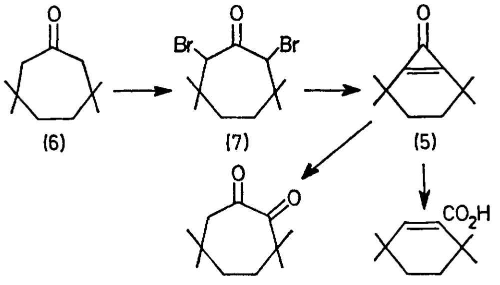
THE strain in cyclopropene[1]† and cyclopropenone undoubtedly imposes a synthetic limitation on the size of the alicyclic ring that can be fused to the three-membered ring system. Thus, an attempted synthesis of the butano-derivative (**1a**) of cyclopropenone *via* a modified Favorskii reaction met with no success,[2] and 7,7-dimethylbicyclo[4,1,0]hept-1(6)-ene exists as such only below $-20°$.[3] We felt that the high reactivity of the system is more responsible for the earlier failures to isolate these compounds than the intrinsic thermodynamic instability, and we therefore investigated this aspect. We record herein the synthesis of the title compound (**5**). While compound (**5**) is indeed thermally stable (recovered unchanged after heating its CH_2Cl_2 solution at 100° for 5 h) in the absence of acid and base, physical and chemical properties of this compound clearly show additional strain in this system.



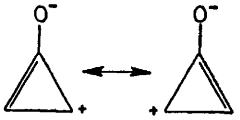
(1)
a; *n* = 4
b; *n* = 5



(2) R = H
(3) R = Me
(4) R = Bu^t



(8) (9)



(C) (D)

Treatment of 3,3,6,6-tetramethylcycloheptanone (**6**)[4] with Br_2 (2 equiv.) provided the corresponding dibromide (**7**) which in turn was dehydrobrominated[5] with KOBu^t in tetrahydrofuran at $-20°$ to give compound (**5**) in 41% yield, m.p. 89·0—89·5°. Elemental analyses and spectral properties are all consistent with the formulation (**5**) (Table).

Two i.r. absorptions characteristic of the cyclopropenone system, one at 1800—1870 cm^{-1} and the other at 1600—1660 cm^{-1}, both shift to lower frequencies as the fused-ring strain increases. The interpretation of these shifts should be reserved until the system is completely analysed, because two modes of vibrations of cyclopropenone are undoubtedly tightly coupled.[6] The hypsochromic shift of the n–π^* absorption in (**5**) is clearly observable as compared with other less strained compounds. In ^{13}C n.m.r. spectra, the signals ascribed to C-1 shift upfield (with allowance for

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† Cyclopropene is estimated to possess *ca.* 56 kcal/mol strain energy.[1]

TABLE. Spectral properties of cyclopropenone derivatives.

Compound	ν_{max} $(CCl_4)cm^{-1}$		λ_{max} (cyclohexane)/nm (ϵ_{max})	δ (^{13}C from Me_4Si; $CDCl_3$)	
				C-1[a]	C-2(C-3)[a]
(2)	1833 1864	—[b]	276 (31)[c]	155·1	158·3[d]
(3)	1848 1866	1657[e]	272 (43)[f]		
(4)	1820 1855	1640[g]		159·5	164·8
(1b)	1840	1540[h]	267 (79)[f]	154·6	164·2
(5)	1790 1852	1617	263 (95)	146·7	169·0

[a] Numbering as for cyclopropenone. [b] R. Breslow, G. Ryan, and J. T. Groves, *J. Amer. Chem. Soc.*, 1970, **92**, 988. [c] R. Breslow and M. Oda, *J. Amer. Chem. Soc.*, 1972, **94**, 4787. [d] Ref. 8. [e] R. Breslow and L. J. Altman, *J. Amer. Chem. Soc.*, 1966, **88**, 504. [f] A. Krebs and B. Schrader, *Annalen*, 1967, **709**, **46**. [g] Ref. 5. [h] Ref. 2.

substituent effects) as the fused-ring size becomes smaller, while the reverse trend is observed for those assigned to C-2 and C-3 [*e.g.*, compare (**5**) with (**4**)]. Being fully aware that the ^{13}C chemical shift is very sensitive to several variables,[7] we interpret these trends as an indication of change in the electron distribution in the system: cyclopropenone is a resonance hybrid[8] and the weight of contribution of each structure to the ground state of the system varies with the nature of the fused-ring. Thus, in (**5**) (C) and (D) become more important than they are in the parent compound. As a result, the double bond becomes more exocyclic (in type) to the fused-ring system, relieving the strain of the entire system as much as possible, and, further, C-2 and C-3 now carry a slightly more positive charge than the corresponding atoms in other compounds such as (**4**). However, the above interpretation is only tentative and obviously is subject to further scrutiny.

While treatment of (**4**) with aqueous 25% NaOH at reflux for 2 h resulted in its recovery in 86% yield[5] and compound (**1b**) underwent ring cleavage only with refluxing, aqueous 10% KOH to provide cycloheptene-1-carboxylic acid,[2] the ring in compound (**5**) opened readily with 0·05N-NaOH in aqueous tetrahydrofuran at room temperature. The hydroxide anion attacks two different sites in cyclopropenone (*cf.* **1b**), providing (**8**) and (**9**) in a 3:2 ratio as the primary products. This result is presumably in line with the above interpretation of the ^{13}C n.m.r. spectra. The instability of (**5**) is also manifested by its sensitivity towards acid. Thus, (**5**) wash completely decomposed upon brief treatment with 0·1N-H_2SO_4 at room temperature, giving a quantitative yield of (**9**). This behaviour contrasts with that of (**1b**), which is stable in 75% H_2SO_4.[2]

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[1] G. L. Closs, *Adv. Alicyclic Chem.*, 1966, **1**, 53.

[2] R. Breslow, J. Posner, and A. Krebs, *J. Amer. Chem. Soc.*, 1963, **85**, 234; R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *ibid.*, 1965, **87**, 1326.

[3] G. L. Closs and W. A. Böll, *J. Amer. Chem. Soc.*, 1963, **85**, 3904.

[4] A. L. Liberman and J. V. Vasina, *Zhur. Org. Khim.*, 1967, **3**, 690.

[5] J. Ciabattoni and E. C. Nathan, III, *J. Amer. Chem. Soc.*, 1969, **91**, 4766.

[6] A. Krebs, B. Schrader, and F. Höfler, *Tetrahedron Letters*, 1968, 5935, and references cited therein.

[7] G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley-Interscience, New York, 1972, ch. 3.

[8] *Cf.* R. C. Benson, W. H. Flygare, M. Oda, and R. Breslow, *J. Amer. Chem. Soc.*, 1973, **95**, 2772.