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Linear Bond Angle–Bond Length Correlation from X-ray Analysis of Tricyclo[2.1.0.0^{2,5}]pentane Derivatives

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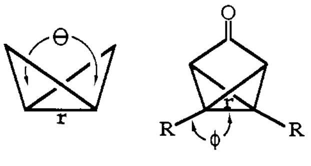
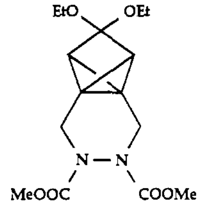
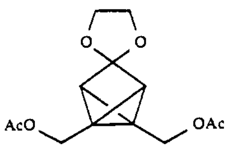
X-ray crystallographic examination of rigidly fixed bicyclobutanes has led to the generalization that the central bond length r depends in a linear fashion on the magnitude of the flap angle θ.[1-5] The bond contraction of r is mirrored in theoretical calculations carried out following the experimental observation.[3,5] In addition, theoretical analysis predicted that r should become longer as the angle ϕ contracts. We now describe a linear correlation, of the bond length r with the external angle ϕ of the substituent, which fully substantiates the theoretical treatment.[3] One of the key elements in this correlation is the propellane **1**. The structural properties of that substance are described, and then the relationship between r and ϕ is treated.





1



2

The propellane **1** contains a bicyclo[1.1.0]butane spanned by a one carbon bridge in the 2- and 4-positions (numbered as shown in Figure 1). Carbon atoms C1 and C5 in **1** are inverted. Their inversion parameters are 168.9° and 168.1°[6] or 0.125 and 0.134 Å.[7] The six-membered ring has a twist conformation as follows: C6–C5–C1–C7, 4.8 (3)°; C1–C5–C6–N1, −18.0 (3)°; C5–C1–C7–N2, −16.9 (3)°; C5–C6–N1–N2, 47.6 (2)°; C1–C7–N2–N1, 45.9 (3)°; and C6–N1–N2–C7, −64.9 (2)°. The geometry of the nitrogen atoms and their substituents corresponds to a flattened pyramid (sum of bond angles: N1, 357.5°; N2, 354.0°).[8]

The interplanar angle θ between the three-membered rings C1, C2, C5 and C1, C4, C5 has a value of 98.6 (2)°, which is close in magnitude to the same angle (96.8°) in the open tricyclo[2.1.0.0^{2,5}]pentane **2**.[2a] Therefore, the influence of the interplanar angle θ on the length of the bridging C1–C5 bond must be the same in both **1** and **2**.[1-5] The bicyclo[1.1.0]butane group in molecules **1** and **2** does not carry conjugating substituents which would influence the C1–C5 bond by electronic effects. Accordingly, since the length (1.509 (2) Å) of the bridging C1–C5 bond in **1** (Figure 1) is significantly longer than the corresponding bond (1.455 Å) in **2**, the difference must be a consequence of the external bond angle.

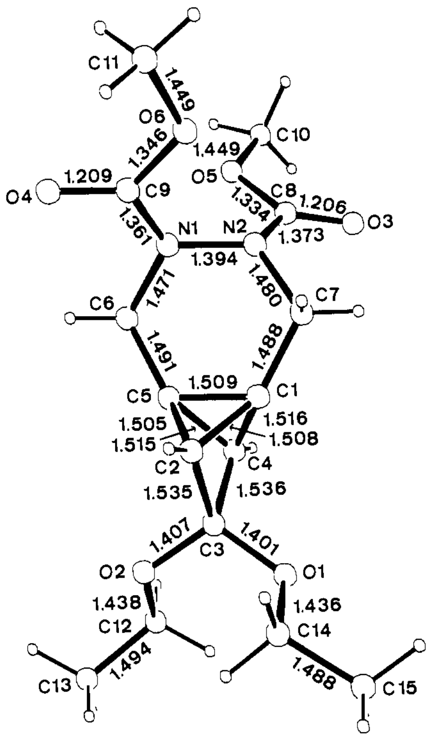
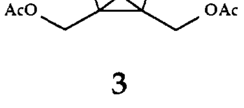


Figure 1. X-ray crystal structure of **1** with bond distances in Å. The estimated standard deviations are 0.002–0.004 Å.

The C7 and C6 carbon atom substituents at the bridgehead atoms C1 and C5 are connected by the nitrogen atoms N1 and N2 in a six-membered ring, and the bond angles C1–C5–C6 and C5–C1–C7 in **1** are compressed to 119.5 (2)° and 120.4 (2)° from the comparable angles of 133.0 (1)° and 132.8 (1)° in the open ketal **2**. Other [4.1.1]propellanes[9] show bond lengths of 1.541 to 1.573 Å between the bridgehead carbons, somewhat longer than the bridging bond length in compound **1** because their angles ϕ (102.0–110.5°) are slightly smaller and their interplanar angles θ (113.2–121.9°) are considerably larger than those in **1**. Both geometric factors cause a lengthening of the central propellane bond.

The ketones **3**[2b] and **4**[1] have the same rigid tricyclo[2.1.0.0^{2,5}]pentane carbon framework system. Compared with the ketals **1** and **2**, the bridging bond lengths r are shortened by the electronic effect of the carbonyl group,[2a] but superimposed on this effect is a striking dependence of the bond length r on the



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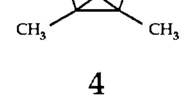

4

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(8) Crystallographic data: a = 12.774 (2) Å, b = 11.978 (3) Å, c = 12.112 (2) Å; β = 114.39 (1)°; space group $P2_1/c$; Z = 4; D_c = 1.28 g/cm^3; diffractometer data (Mo Kα radiation, graphite monochromator, sin $\theta/\lambda \leq$ 0.66 Å^{-1}): 4049 unique reflections, 1781 observed ($I > 3\sigma(I)$); full matrix refinement: R = 0.036. Further details of the crystal structure investigation may be obtained as Supplementary Material.

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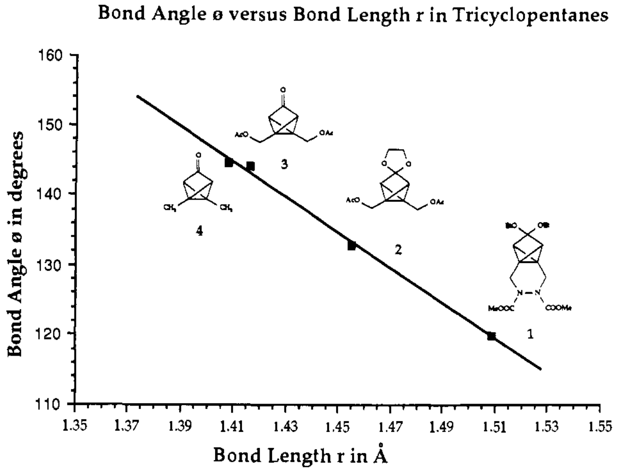

Figure 2. Plot of bond length r versus external angle in tricyclo[2.1.0.0^{2,5}]pentanes ($r = 0.998$).

angle ϕ. The inverse relationship between the bridging bond length r and the bridgehead substituent angle ϕ (C1–C5–C6 and C5–C1–C7 for **1**) is apparent in the linear correlation ($r = 0.998$) between the length of the bridging C1–C5 bond r and the angle ϕ shown in Figure 2. This plot constitutes clear and direct confirmation of the theoretical prediction[3] and the qualitative suggestion[6] that the angle ϕ is a direct determinant of the bridging bond length in bicyclobutanes.

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Supplementary Material Available: Table I, atomic coordinates and thermal parameters of **1**; Table II, interatomic angles of **1**; Table III, anisotropic thermal parameters for **1**; Table IV, atomic coordinates and thermal parameters of H-atoms (3 pages); Table V, structure amplitudes (26 pages). Ordering information is given on any current masthead page.

Free Radical Ring Expansion by Three and Four Carbons

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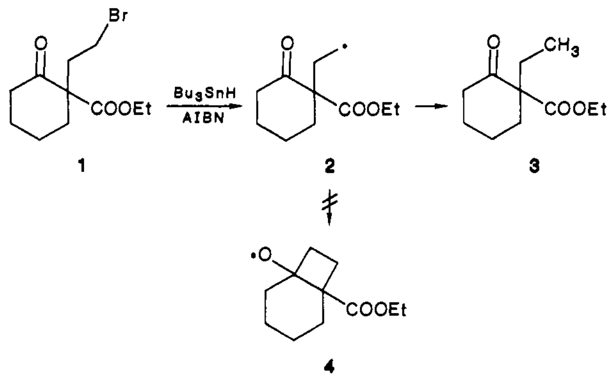
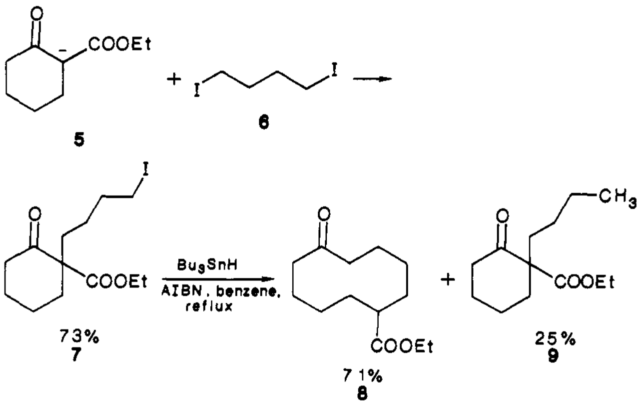
Organic synthesis[1] requires efficient and flexible access to functionalized medium-sized rings. In this paper, we describe a new route to medium-sized rings based upon free radical promoted insertion of a three- or four-carbon chain into a cyclic β-keto ester system. The new reaction is an extension of the recently discovered one-carbon ring expansion reaction of α-(bromomethyl)-β-keto esters with tri-n-butyltin hydride as the promoting reagent,[2-4] but the new reaction is itself unique among ring expansion methods.

We doubted that a two-carbon ring expansion could be carried out. Indeed, when the bromoethyl-substituted β-keto ester **1** is treated with tri-n-butyltin hydride in the presence of AIBN in refluxing benzene, no ring-expanded product is observed; only the ethyl-substituted β-keto ester **3** is obtained. Apparently, formation of the four-membered intermediate **4** required for ring-expansion is not competitive with chain transfer reduction of the initially formed radical **2**.



By contrast, the three-carbon and four-carbon ring expansions appear to be very promising. When the bromo- or iodopropyl or the bromo- or iodobutyl derivatives are treated with tri-n-butyltin hydride,[5] smooth ring expansion occurs to yield the enlarged ring together with a small amount of reduction product. To illustrate: ethyl cyclohexanone-2-carboxylate (**5**) was treated with 1,4-diiodobutane (**6**) in the presence of sodium hydride yielding the 2-iodobutyl adduct **7** (73%). When **7** was treated with tri-n-butyltin hydride, ethyl cyclodecanone-6-carboxylate (**8**) was produced in 71% yield together with the direct reduction product ethyl 2-butylcyclohexanone-2-carboxylate (**9**) (25%).



Further examples are presented in Table I. The ring expansion product is readily separated from the direct reduction product by column chromatography since the large ring products elute significantly more slowly than do the direct reduction products.

Iodides undergo more efficient chain transfer with the tri-n-butyl radical than do the corresponding bromide; therefore, iodides give higher yields of ring-expansion product, in accord with the observations of Porter.[6]

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(3) A similar transformation, carried out simultaneously with our work,[2] was reported very recently by Beckwith, A. L. J.; O'Shea, D. M.; Gerba, S.; Westwood, S. W. *J. Chem. Soc., Chem. Commun.* **1987**, 666. This paper also contains an example in which a phenyl radical undergoes intramolecular insertion into a β-keto ester resulting in formation of a benzocyclodecanone as one of the products. See, also: Okabe, M.; Osawa, T.; Tada, M. *Tetrahedron Lett.* **1981**, 1899. Tada, M.; Miura, K.; Okabe, M.; Seki, S.; Mizukauni, H. *Chem. Lett.* **1981**, 33. Best, W. M.; Cook, A. P. F.; Russell, J. J.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1139.

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(5) The tri-n-butyltin hydride is delivered in low concentration by using a syringe pump.

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