The values of log $k_p^{R_m}$ calculated in Table I are in good agreement with the experimental values; we have assumed here that the interaction term i is negligible.[8,9]

Path 16, in which both environments differ from that of ketone I, leads to an experimental value of log $k_p^{R_m}$ in accord with the calculated value. The partial rate constant for the methyl group observed for this path lies at the intersection of two lines parallel to the lines A Me and Op Me. Thus, if the interaction terms can be neglected, the experimental values must be situated at the nodes of the net made up of lines A and Op, each line representing a family of environments. This net thus formed is characteristic of the migrant group.

We suggest that it will be possible to deduce from a series of nets not only the importance and the sense of the interaction terms, but also parameters belonging to each migrant group. Such parameters should lead to a more general and more precise method of correlating alkyl group migrating tendencies in carbonium ion rearrangements.

Acknowledgment. We thank Dr. J. S. Lomas for helpful discussions and Mrs. S. Briand for technical assistance.

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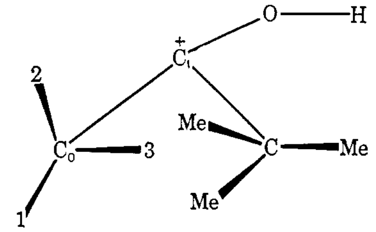
[8] From the position of point 6 with respect to the line A Me, we deduce that the interaction is nonzero. It seems most likely that this is a statistical effect arising from the existence of preferred conformations of the hydroxy carbonium ion.



To minimize the interaction between the substituents at C_0 and the t-butyl group, the methyl group will tend to occupy position 3 in preference to position 1 or 2. We assume that the migrant group occupies a position such that the C_0–R_m bond is coplanar with the axis of the vacant p orbital of the electron-deficient carbon atom. Clearly migration by path 6 is inhibited.

[9] Point 11 lies off the line Op Me; however, if we decrease by one unit the number of carbon atoms making up the environment of C_t, this point can be adjusted to its expected position. This suggests that the contribution of the environment becomes zero beyond the position δ with respect to C_0. This hypothesis remains to be verified.

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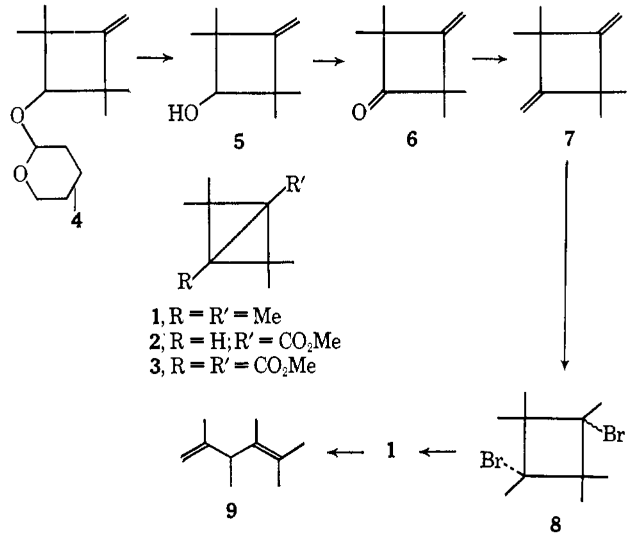
Hexamethylbicyclo[1.1.0]butane

Sir:

Consideration of a model[1] of the title compound **1** suggests that, besides the strain inherent in bicyclo[1.1.0]-butane,[2] there would also be present nonbonded methyl group interactions which should appreciably increase the energy content of such a molecule relative to the parent compound. The two *endo* methyl groups are held in a pseudo-1,3-diaxial relationship to one another, and the four remaining methyl groups are in configurations which are mutually almost totally eclipsed, although at a somewhat more divergent angle than in aliphatic systems.

Recently, we reported[3] the synthesis of methyl 2,2,-4,4-tetramethylbicyclo[1.1.0]butanecarboxylate[4] (**2**) by an intramolecular alkylation reaction.[5] We now wish to report the preparation of the fully substituted hexamethylbicyclo[1.1.0]butane (**1**) by an intramolecular Wurtz reaction.[6]

Scheme I



3-Methylene-1-tetrahydropyranyloxy-2,2,4,4-tetramethylcyclobutane[3] (**4**) was converted by methanolysis to the methylene alcohol **5**:[7] (67%); mp 48–49°; ν_{max}^{Nujol} 3300, 3070, 1660, 880 cm^{-1}. Oxidation by chromic acid in ether[8] or acetone[9] gave the keto methylene compound **6**:[7] (51%); mp 42–43°; $\nu_{max}^{CCl_4}$ 3080, 1800, 1675 cm^{-1}; uv,[10] $\lambda_{max}^{cyclohexane}$ 214 mμ (ϵ 2000), 302 (22), 316 (26), with shoulders at 293, 328 mμ; nmr, δ (CCl_4) 5.00 (s), 1.21 (s) ppm (ratio 1:6). Compound **6** on treatment with methylenetriphenylphosphorane in ether gave the dimethylene compound **7**:[7] (78%); mp 66–68°; ν_{max}^{Nujol} 3070, 1650, 880 cm^{-1}; nmr (CCl_4), δ 4.80 (s), 1.22 (s) ppm (ratio 1:3). The dimethylene compound **7** reacted with liquid hydrogen bromide to produce 1,3-dibromohexamethylcyclobutane (**8**)[7] which crystallized from hexane as a 1:2 mixture of *cis* and *trans* isomers (59%):[7] mp 217–220° dec; nmr (CCl_4), three peaks of equal intensity at δ 1.04, 1.56, 1.89 ppm (*cis* isomer) and two peaks in the ratio 2:1 at δ 1.33, 1.91 ppm (*trans* isomer). When the mixture of dibromo isomers **8** was stirred under nitrogen in dimethoxyethane with an excess of sodium–potassium alloy

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[1] The model is based on the dimensions considered for bicyclo-[1.1.0]butane by M. D. Harmony and K. Cox, *J. Amer. Chem. Soc.*, **88**, 5049 (1966).

[2] K. B. Wiberg, G. M. Lampman, R. P. Cuila, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965). These authors estimate the strain energy as 64 kcal/mol.

[3] C. Burridge and D. P. G. Hamon, *Chem. Commun.*, 206 (1968).

[4] Two other tetramethyl compounds have recently been reported: (a) the 1,3-dimethyl dicarboxylate compound **3** by M. F. Neumann, *Angew. Chem. Intern. Ed. Engl.*, **6**, 79 (1967); E. J. Corey and M. Jautelat, *J. Amer. Chem. Soc.*, **89**, 3912 (1967); (b) the 1,3-dichloro compound by M. R. Rifi, *ibid.*, **89**, 4442 (1967).

[5] K. B. Wiberg and R. P. Cuila, *ibid.*, **81**, 5261 (1959).

[6] K. B. Wiberg and G. M. Lampman, *Tetrahedron Lett.*, 2173 (1963).

[7] Analytical data were consistent with this formula.

[8] H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, **83**, 2952 (1961).

[9] A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2555 (1953).

[10] These values agree favorably with those found for 3-methylenecyclobutanone: P. Dowd and K. Sachdev, *J. Amer. Chem. Soc.*, **89**, 715 (1967).

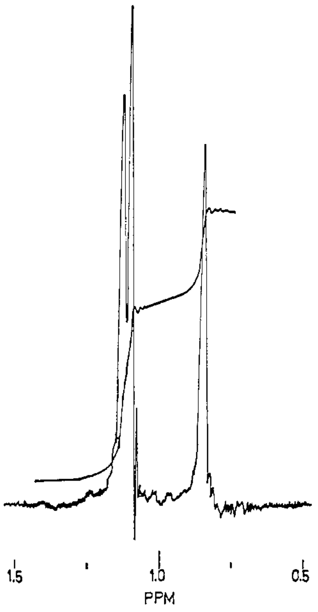

Figure 1.

at *ca.* 50° for 3 hr, hexamethylbicyclo[1.1.0]butane (**1**) was formed. This was substantiated by the following evidence. Partitioning of the above reaction mixture between carbon tetrachloride and water, followed by several washes of the carbon tetrachloride solution with water, gave a solution, the nmr spectrum of which is recorded in Figure 1. The model of compound **1** suggests that there are three pairs of methyl groups which could exist in different magnetic environments: the angular, the *exo*, and the *endo* methyl groups. The assignment of resonances to these groups is not clear-cut. The ring methyl groups in the monoester **2**[3] resonate at δ (CCl$_4$) 1.25 and 1.30 ppm, while those in the diester **3**[4a] occur at δ (CDCl$_3$) 1.44 and 1.48 ppm.[11] It would appear therefore that the *exo* and *endo* methyl groups are affected to the same extent by the addition or subtraction of a carbomethoxy group. In the as yet unknown 2,2,4,4-tetramethylbicyclo[1.1.0]butane the methyl groups might therefore be expected to resonate at *ca.* δ 1.12 and 1.06 ppm. Introduction of angular methyl groups might be expected to cause shielding[12] of the hydrogens of the *exo* methyl groups and those of the introduced groups by approximately an equal amount. This could account for the difference in chemical shift between the position found for the angular methyl groups in 1,3-dimethylbicyclo[1.1.0]butane[13] (δ 1.34 ppm) and the present compound (δ <1.12).[14]

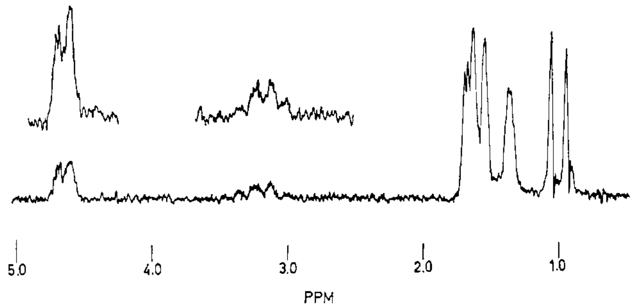

Figure 2.

The peak at δ 0.85 ppm would then be assigned to the shielded *exo* methyl groups. The nmr spectrum is thus consistent with the proposed structure.

Further evidence for this structure became available after attempted purification of the compound. Glpc of either the dimethoxyethane solution or the carbon tetrachloride solution showed one major peak other than those for solvents. Collection[15] of the compound corresponding to this major peak afforded 2,3,4,5-tetramethylhexa-1,4-diene[7] (**9**). The structure for this compound is confirmed by the nmr spectrum (CCl$_4$)[16] (Figure 2). The multiplet at δ 4.7 ppm is assigned to the vinylic hydrogens of the terminal olefin. The broadened quartet at δ 3.2 ppm is assigned to the hydrogen at C-3, and the doublet at δ 1.0 ppm is assigned to the methyl group at C-3. The remaining peaks fit the pattern expected for the four methyl groups on double bonds. The structure is also supported by the mass spectrum which showed a molecular ion at *m/e* 138, the base peak at *m/e* 123 (M − 15), which corresponds to the loss of the C-3 methyl group to give a doubly allylic cation, and other prominent fragmentations consistent with the proposed structure.

In an attempt to study the half-life for the rearrangement of compound **1** to **9** in solution, **1** was extracted into *o*-dichlorobenzene. This solution was heated either in the probe of the nmr machine (almost completely converted to **9** in 1 hr at 120°) or externally (*ca.* 25% converted to **9** in 0.5 hr at 130°). These results show that **1** has reasonable thermal stability, but the inconsistency between measurements, coupled with the gas chromatographic results, suggests that the decomposition may be surface dependent.

Bicyclo[1.1.0]butane systems are reported to rearrange by a concerted mechanism to conjugated dienes.[17] The rearrangement reported above is therefore novel, but still consistent with the proposed structure.

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[11] The difference between CDCl$_3$ and CCl$_4$ as solvent is assumed to be small (see N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 159).

[12] For a discussion of the diamagnetic anisotropy of the C–C single bond see L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Ltd., London, 1959, p 117.

[13] W. von E. Doering and J. F. Coburn, Jr., *Tetrahedron Lett.*, 991 (1965).

[14] The angular methyl groups could be labeled by the use of deuterium bromide. It is hoped that more information will be available when the full paper is written.

[15] A 10-ft glass column was packed with 20% SE 30 on 60–80 Firebrick; the column and injector temperatures were 100°. Rearrangement occurred even at 50° on a 3-ft column.

[16] The nmr spectrum of 2,3,4,5-tetramethylhexa-2,4-diene has been reported to consist of two somewhat broadened singlets in the ratio 1:2 at δ 1.48 and 1.63 ppm: R. Criegee, U. Zirngibl, H. Furrer, D. Seebach, and G. Freund, *Chem. Ber.*, **97**, 2942 (1964).

[17] K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968).