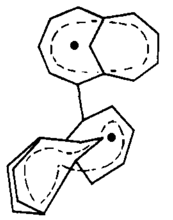
anything else. If this is the case, then there must be a mechanism for fulvalenes such as **9** to close to dimethylenecyclobutanes with the stereochemistry expected to diradicals such as **14**. One way to resolve this apparent dichotomy is a relatively facile rotation about the adjoining fulvalene double bonds which would interconvert the fulvalenes and the diradicals.[18] Of course one important consequence of this suggestion is that the structures of the dimers can say nothing about the structures of the monomers.



14

Finally, it is interesting to explore why the double bonds in **13** are localized as suggested. Models clearly show that the proposed structure is much less strained than the alternative.

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(13) In general, when the conjugation of a bicyclo[5.4.1]dodecapentaene is either broken by a saturated group (e.g., CH_2)[14] or perturbed by a localizing group (e.g., $C{=}O$)[9,15] those isomers containing a cycloheptatriene moiety (as **1** or **7**) seem to be more stable than those containing the dimethylenecycloheptadiene moiety (as **3**). This preference has been attributed to strain and a combination of strain and homobenzenoid stabilization of the cycloheptatriene.[4,16]
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(18) By this mechanism the absence of **11** is explained because **9** and **11** could close to the same cyclobutanes. **12** is too strained to be expected.

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Carbon-13 and Proton Hyperfine Splittings and Their Variation with Temperature for Some Alkoxyalkyl Radicals[1]

Sir:

Successive replacements of the hydrogen atoms in the planar $\dot{C}H_3$ radical by fluorine yields radicals with increasing $^{13}C_\alpha$ hyperfine splitting constants.[2] A similar phenomenon is anticipated for successive substitution of H by RO groups (R = H or alkyl). While there is a wealth of data relating to the $a(^{13}C_\alpha)$ values of monoalkoxyalkyls,[3-8] there are no such data for trialkoxymethyls and the only data relating to dialkoxyalkyls involve the radical anion of perdeuterioacetic acid in a solid matrix[9] and some five- and six-membered cyclic radicals.[6,10] Since ring strain induces deviations from planarity at C_α[5,11] and since this leads to enhanced $a(^{13}C_\alpha)$ values we have now measured $a(^{13}C_\alpha)$ for some neutral acyclic dialkoxyalkyls and for trimethoxymethyl in solution.

Our present results are compared with data from the literature in Table I. As was expected, $a(^{13}C_\alpha)$ increases with increasing substitution by RO, but the effect is less than with fluorine.[12] The similarity in $a(^{13}C_\alpha)$ values for all dialkoxyalkyls indicates that these values are not significantly influenced by ring strain in the five- and six-membered rings. The values of $a(^{13}C_\alpha)$ for the di- and trialkoxyalkyls support the view that these radicals are nonplanar.

The temperature dependence of the hyperfine coupling constants, $a(^{13}C_\alpha)$ and $a(H_\alpha)$, can yield important information regarding the configuration[13] of the radical in question,[11,14,15] since the variation in a with temperature arises primarily from out-of-plane vibrations at C_α. Thus, it is generally agreed that if $[\partial|a(^{13}C_\alpha)|/\partial T]_{T\rightarrow 0}$ is negative (cf. $(Me_3CO)_2\dot{C}H$ and $\overline{OCH_2OCH_2O\dot{C}}H$) the radical prefers a nonplanar configuration.[14-16] The sign of $\partial|a(H_\alpha)|/\partial T$, (and of the deuterium isotope effect)[17] has occasionally been used to deduce the sign of $a(H_\alpha)$.[11,19,20] We wish to draw attention to the fact that although the sign of $\partial|a(H_\alpha)|/\partial T$ is not an entirely reliable guide to the sign of $a(H_\alpha)$,[15] its sign for alicyclic $(RO)_2\dot{C}H$ radicals (−) is more consistent with $a(H_\alpha) > 0$ than with $a(H_\alpha) < 0$.[21]

For nonplanar radicals having inversional symmetry the out-of-plane vibrations are governed by a symmetric double-minimum potential function.[14,15] The temperature dependence of $a(^{13}C_\alpha)$ and of atoms directly bonded to C_α (e.g., H_α) have been discussed (with special reference to $(CH_3)_3\dot{C}$) by Wood and co-workers[14] and by Krusic and Meakin.[15] According to the general theory of the latter authors,[15] which utilizes a potential function of the form $V(q) = -aq^2 + bq^4$ $(a, b > 0)$, the sign of $\partial|a(H_\alpha)|/\partial T$ will depend not only on the sign of $a(H_\alpha)$, but also on the number of vibrational states below the top of the inversion barrier *and* on the temperature of the measurements. For example, for $a(H_\alpha) > 0$, if there are at least three vibrational levels below the barrier top then $\partial|a(H_\alpha)|/\partial T$ will be negative at low and positive at high temperatures,[22] while if there are only two vibrational states below the barrier then $\partial|a(H_\alpha)|/\partial T$ will, because of zero-point effects, be positive at all temperatures.[15,23] The reverse applies if $a(H_\alpha) < 0$.

For the specific case of alicyclic $(RO)_2\dot{C}H$ radicals, the magnitude of the $a(^{13}C_\alpha)$ values indicates that the radicals are severly bent while the negative sign of $\partial|a(^{13}C_\alpha)|/\partial T$ for $(Me_3CO)_2\dot{C}H$ implies that, for this radical at least, there must be three or more vibrational levels below the barrier top[15] and, moreover, the experimental measurements must have been made in the low temperature[22] region. The fact that $\partial|a(H_\alpha)|/\partial T$ is *negative* therefore requires that $a(H_\alpha)$ is *positive* for these radicals.[25]

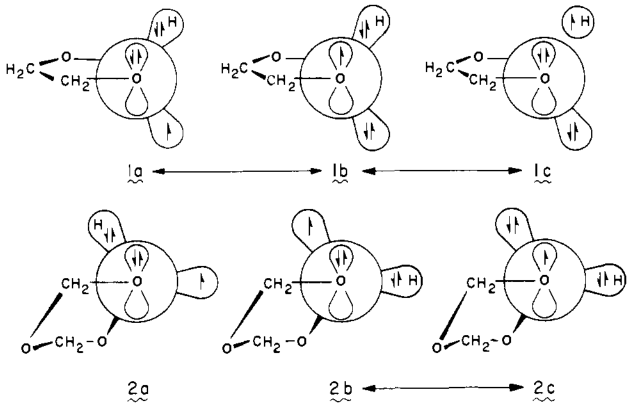
Finally, the magnitudes of $a(H_\alpha)$ in alicyclic $\overline{(RO)_2\dot{C}H}$ (9.6-14 G), in $\overline{OCH_2CH_2O\dot{C}}H$ (21.7 G), and in $\overline{OCH_2O}$-

Table I. Hyperfine Splitting Constants (G) for Some Alkoxymethyl Radicals

Radical	$a(^{13}C_\alpha)$, °C[a]	$\partial\|a(^{13}C_\alpha)\|/\partial T$[b]	$a(H_\alpha)$, °C[a]	$\partial\|a(H_\alpha)\|/\partial T$[b]	Ref
$\dot{C}H_3$	38.34 (−177)	+13.5	−23.04 (−177)	−1.3	c
$HO\dot{C}H_2$	45.33 (−79)	+22.0	−17.65[d] (−125)	−4.7	7
			−18.53[d]		
$CH_3O\dot{C}H_2$	47.2 (20)		−16.8[d] (−100)[e]		8
			−18.3[d]		
$(CH_3)_3CO\dot{C}H_2$	f		−16.5[d] (−130)	−6.0	This work[g]
			−18.2[d]		
$HO\dot{C}(H)CH_3$	54.1 (20)		−15.0 (20)		8
$HO\dot{C}(CH_3)_2$	65.05 (−29)				3
$DO\dot{C}(O^-)CD_3$	114 (−196)				9
$(HO)_2\dot{C}H$	101.1 (−29)		13.50 (−29)		This work[h]
			14.00 (−33)[i]	−38[i]	
$(CD_3O)_2\dot{C}H$	97.9 (−118)	j	12.32 (−116)	−6.0	This work[g]
$(Me_3CO)_2\dot{C}H$	91.54 (−120)	−11.0	9.64 (−100)[k]	−28.5	This work[g]
$\overline{OCH_2OCH_2O\dot{C}}H$	99.8 (20)		0.47 (20)	−3.7[l]	6
	97.83 (−40)	−2.8	0.27 (−40)	−0.5	This work[g,m]
$\overline{OCH_2OCH_2O\dot{C}}CH_3$	107.5 (20)				6
$\overline{OCH_2CH_2O\dot{C}}H$	103.0 (20)		21.9 (20)		10
			21.72 (−120)	−1.9	This work[g]
$\overline{OCH_2CH_2O\dot{C}}CH_3$	110 (20)				10
$(MeO)_3\dot{C}$	152.7 (−120)	j	n		This work[g]

[a] Temperature of measurement. [b] mG/deg. [c] R. W. Fessenden, *J. Phys. Chem.*, 71, 74 (1967). [d] The two H_α are not magnetically equivalent at low temperatures. [e] Reference 36. [f] Not resolved. [g] Generated by H abstraction using photochemically produced $Me_3CO^\cdot$ in cyclopropane. [h] Generated by the method used in footnote *i*. [i] H. Hefter and H. Fischer, *Bunsenges. Phys. Chem.*, 74, 493 (1970). [j] Small, the spectrum at −80 °C was too weak to determine $a(^{13}C_\alpha)$ accurately. [k] The value of $a^{H\alpha}$ was misquoted in ref 19: $a^{H\alpha}$ = 10.1 G at −110 °C, not 11.1 G as reported. [l] From data of H. Yoshida and B. Ranby, *Acta Chem. Scand.*, 19, 145 (1965). [m] The difference between the values of $a^{13C\alpha}$ and $a^{H\alpha}$ reported and those in ref 6 is probably to be attributed to a solvent effect, rather than a temperature effect. [n] a^H (9 H) = 0.36 G.

Scheme I



$\overline{CH_2O\dot{C}}H$ (0.3 G) deserve comment. The similarity in $a(^{13}C_\alpha)$ for these radicals implies that the variations in their $a(H_\alpha)$ values cannot be mainly due to changes in configuration, as previously suggested.[6] Assuming that the two lone pairs on oxygen are not equivalent[28] and that the C_α semioccupied orbital interacts only with the *p*-type lone pair,[30] the possibility for conjugative delocalization of the unpaired electron will be maximized in $\overline{OCH_2CH_2O\dot{C}}H$, i.e., **1a** ↔ **1b**.[31] As a consequence, the value of $a(H_\alpha)$ for this radical will be *enhanced* because *positive* spin will be transmitted to H_α by *back-hyperconjugation from the oxygens' p-type lone pairs*,[33] i.e., **1b** ↔ **1c**.[34] In contrast, in 1,3,5-trioxane (which exists in a chair conformation[35]) the abstraction of an equatorial H will lead to an $\overline{OCH_2OCH_2O\dot{C}}H$ radical in which the orbitals of the β-oxygens' p-type lone pairs and the C_α semioccupied orbital are orthogonal,[34] i.e., **2a**. As a consequence, conjugative delocalization is not expected and since there can then be no back-hyperconjugation to H_α, $a(H_\alpha)$ is small. Alternatively, abstraction of an axial H (which is equivalent to inversion at C_α) gives a radical in which conjugative delocalization can occur, i.e., **2b** ↔ **2c**, but back-hyperconjugation cannot because the oxygen p-type lone pairs and the C_α-H_α bond are orthogonal. Therefore, $a(H_\alpha)$ will be small in either conformation of the $\overline{OCH_2OCH_2O\dot{C}}H$ radical. (We note, in passing, that the radical reactions of trioxane and of other oxygen containing six-membered ring compounds are expected to be highly stereospecific.) The conformationally more mobile acyclic radicals have intermediate $a(H_\alpha)$ values, the large temperature coefficients for which can be attributed to decreased ease of rotation about the RO-C_α bonds at low temperatures.[7,36] That is, lowering the temperature improves conjugative delocalization of the unpaired electron from C_α, to O and this, by increasing bending at C_α[6,8,32] *and* by back-hyperconjugation, makes $\partial|a(H_\alpha)|/\partial T$ larger for alicyclic than for cyclic radicals.

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(12) The $a(^{13}C_\alpha)$ values in the two classes of radicals can be correlated by the equation, $a(^{13}C_\alpha)\,[(RO)_n\dot{C}H_{3-n}] = 19.5 + 0.49\,a(^{13}C_\alpha)\,[F_n\dot{C}H_{3-n}]$ (n = 0, 1, 2, 3) but this does not allow the relative effectiveness of RO and F at inducing bending to be determined (cf. ref 6).

(13) Configuration here is used to describe the geometry of the radical center.[11]

(14) J. B. Lisle, L. F. Williams, and D. E. Wood, *J. Am. Chem. Soc.*, **98**, 227 (1976), and references cited.

(15) P. J. Krusic and P. Meakin, *J. Am. Chem. Soc.*, **98**, 228 (1976).

(16) For low inversion barriers, $a(^{13}C_\alpha)$ may not exhibit a negative temperature coefficient.[15]

(17) Replacing H_α by deuterium will reduce the amplitude of out-of-plane vibrations and so will produce an effect similar to that obtained by reducing the temperature. The following discussion of $\partial|a(H_\alpha)|/\partial T$ is therefore applicable to the deuterium isotope effect defined by[11,18] $|a(H_\alpha)| - 6.5144|a(D_\alpha)|$.

(18) The H/D nuclear moment ratio is 6.5144.

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(21) For other evidence favoring $a(H_\alpha) > 0$, see ref 8. Contrary conclusions are contained in ref 5, 6, and 19.

(22) Low and high temperature must be defined in terms of barrier height.[15]

(23) Using the theory and notation of ref 15 and truncating its eq 6 after the second term, yields for $a(H_\alpha) > 0$:

$$a(H_\alpha, \theta) = -|a_0| + a_2\alpha_m{}^2F_2(\theta, E_0) > 0$$

The temperature coefficient measured at two temperatures near θ where $a(H_\alpha)$ is still positive ($\theta_1 < \theta < \theta_2$), is given by

$$\mathrm{d}|a(H_\alpha)|/\mathrm{d}\theta = \frac{a_2\alpha_m{}^2}{\Delta T}\left[F_2(\theta_2, E_0) - F_2(\theta_1, E_0)\right]$$

Inspection of the curves[15] for F_2 reveals that with $\geqslant 3$ vibrational levels $\mathrm{d}|a(H_\alpha)|/\mathrm{d}T < 0$ at low[24] and >0 at high temperatures,[22] while for 2 levels $\mathrm{d}|a(H_\alpha)|/\mathrm{d}T > 0$ at all temperatures.

(24) With these conditions the same conclusion can be deduced qualitatively for any double minimum potential function that has inner walls less steep than outer walls since the radical will become more bent as the temperature decreases and so H_α will acquire more positive spin.

(25) The opposite situation probably obtains with 7-norbornenyl for which it had been suggested[20] that $a(H_\alpha) > 0$ because the temperature coefficient and isotope effect[17] were positive. However, other studies[26] have indicated that $a(H_\alpha) < 0$ which is readily explicable[27] if the out-of-plane vibrations are governed by an asymmetric double-minimum potential function.

(26) T. Kawamura, Y. Sugiyama, M. Matsunaga, and T. Yonezawa, *J. Am. Chem. Soc.*, **97**, 1627 (1975).

(27) Footnote 11, ref 26.

(28) Photoelectron spectroscopy indicates that one lone pair is essentially a pure p-type orbital and the second lone pair is roughly an s-type orbital.[29] The p-type lone pair is of higher energy (lower I.P.) than the s type by $\geqslant$10 eV.

(29) See, e.g., D. A. Sweigart and D. W. Turner, *J. Am. Chem. Soc.*, **94**, 5599 (1972); D. A. Sweigart, *J. Chem. Educ.*, **50**, 322 (1973).

(30) The orbital energies of the unpaired electron and of the p-type lone pair are of similar magnitude.

(31) The role that such overlap plays in producing nonplanarity at C_α and influencing the magnitude of $a(H_\alpha)$ via this bending has been discussed in ref 6 and 32.

(32) See, e.g., R. C. Bingham and M. J. S. Dewar, *J. Am. Chem. Soc.*, **95**, 7182 (1973); P. J. Krusic and R. C. Bingham, *ibid.*, **98**, 230 (1976); F. Bernardi, N. D. Epiotis, W. Cherry, H. B. Schlegel, M. H. Whangbo, and S. Wolfe, *ibid.*, **98**, 469 (1976).

(33) The same conclusion will be reached if the common, but probably unrealistic,[29] assumption is made that the oxygens are sp^3 hybridized with two lone pairs of equal energy.

(34) For simplicity C_α is assumed to remain sp^3 hybridized in the radical. In the Newman projections, the dihedral angles between the O $2p_z$ direction and both the C_α–H_α bond and the C_α half-filled orbital are 30°.

(35) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Wiley, New York, N.Y., 1965, p 251.

(36) A. Hudson and K. D. J. Root, *Tetrahedron*, **25**, 5311 (1969).

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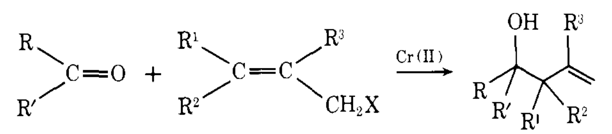
Grignard-Type Carbonyl Addition of Allyl Halides by Means of Chromous Salt. A Chemospecific Synthesis of Homoallyl Alcohols

Sir:

We wish to communicate that chromic chloride is easily reduced by a half molar equivalent of lithium aluminum hydride in tetrahydrofuran (THF) and the resulting salt, presumably Cr(II), can be utilized in the title reaction with high chemospecificity.



Lithium aluminum hydride (44 mg, 1.2 mmol) was added portionwise to anhydrous chromic chloride[1] (370 mg, 2.3 mmol) suspended in THF (5 mL) at 0 °C under an argon atmosphere. Spontaneous hydrogen evolution was observed, and a dark brown suspension was obtained.[2] To this suspension benzaldehyde (92 mg, 0.86 mmol) and subsequently prenyl bromide (173 mg, 1.2 mmol) dissolved in THF (5 mL) were added dropwise, and the mixture was stirred for 2 h at room temperature. Aqueous quenching, ether extraction, drying (Na_2SO_4), and distillation (Kugelrohr) gave an oil (124 mg, 82% yield based on benzaldehyde), bp (bath) 105–110 °C (0.12 mm): IR (neat) 3425, 3075, 3035, 1638, 1602, 1494, 1020, 1000, 910, 730, 702 cm^{-1}; NMR (CCl_4) δ 0.94 (s, 3 H), 0.99 (s, 3 H), 1.70 (br s, 1 H), 4.34 (s, 1 H), 4.8–6.2 (m, 3 H), 7.26 (s, 5 H); MS *m/e* 107 (base peak), no 176 (M^+).[3] The reagent prepared as above could be stored under an inert atmosphere in a refrigerator for more than a month without appreciable loss of its activity. The salt prepared from 2 M chromic chloride and 1 M lithium aluminum hydride was found most effective. When the ratio was larger than two, the yield of the adduct decreased, whereas a 1:1 mixture resulted in the reduction of the carbonyl group by the excess hydride. As the commercially available anhydrous chromous chloride (Research Organic/Inorganic Chemical Corp.) is also effective for the reaction (89% (GLC) yield of the product), the active species in the above reaction will be chromous ion. The results of the reaction between allylic halides (or tosylate) and carbonyl compounds are summarized in Table I, which shows that the reaction is general and applicable to a wide variety of both components.

As seen from the table the more substituted γ carbon of an allyl group was attached to the carbonyl carbon.[4] Two molar equivalents of chromous salt were required for the reduction of allyl halide. Although stoichiometric allyl halide was sufficient for the reaction (run 1 and 2), excess halide was much more effective (cf. run 3, 9, and 15). This is ascribed to the homocoupling of the halide,[5] the side products being easily removed by simple distillation or short-column chromatography.

The cyclohexanone/prenyl bromide reaction gave satisfactory yields only in dimethylformamide (DMF) (run 3), which dissolved the Cr(II) salt and probably enhanced the reducing ability of the salt.[6] The aprotic polar solvent was particularly indispensable for the reaction of allyl chloride and tosylate, which were not reduced effectively in THF (run 12 and 13).

A striking feature of the reaction is the high stereoselectivity and chemospecificity. In general, aldehydes were more reactive than ketones. Based on this reactivity difference we could attain selective attack on an aldehyde carbon of a polycarbonylated compound (run 16).[7] Furthermore, the Cr(II)-reduced allyl bromide could discriminate 2-heptanone from 4-heptanone. Noteworthy is the fact that only a single diastereomer