tetroxacyclohexane ring of PDP and CHDP molecules can exhibit a certain rigidity similarly to some derivatives of cyclohexanone diperoxide molecules,[16] rendering the adduct formation less likely.

Conclusions

1. The activation parameters of the thermal decompositions of some substituted tetroxacyclohexane derivatives in organic solvents have been correlated through isokinetic relationships to validate the existence of solvent effects on the unimolecular reactions. Then, the solvating properties of the media help the peroxidic bond rupture of this type of molecules.

2. A true "isokinetic relationship" is only warranted for the ACDP thermolysis which indicates that their reactions constitute a "reaction series" with similar "interaction mechanisms". These can be related to the capacity for hydrogen bonding between the solvent and the diperoxide molecules.

3. In PDP and CHDP thermolyses the solvent effects are less remarkable because their molecules show relatively more important steric hindrance.

Experimental Section

Materials. The ACDP, CHDP, and PDP diperoxides were prepared by methods described elsewhere[17] and their purity was checked by GC and IR analysis (KBr, Nujol). Organic solvents were commercial analytical reagents purified by standard techniques, except the 2-propanol and acetic acid solvents which were distilled from ethylenediaminetetracetic acid (EDTA) to remove traces of metallic ions.

Kinetic Methods. Pyrex glass tubes (8 cm long × 8 mm o.d.), half filled with the appropriate diperoxide solution, were thoroughly degassed under vacuum at −190 °C and then sealed with a flame torch. To perform the runs, they were immersed in a thermostatic silicone oil bath (±0.1 °C) and withdrawn after selected times, stopping the reaction by cooling at 0 °C. The diperoxides remaining in the reaction solution were determined by quantitative GC analysis (internal standard method, *n*-octane) using a silica fused capillary column (HP-SP-2100, 30 m × 0.25 mm i.d.) installed in a 5840 A Model Hewlett-Packard instrument, with nitrogen as the carrier gas and FID detection. The corresponding first-order rate constant values were obtained by least mean squares treatment of the data plotting the values of ln [diperoxide] vs time. In previous isopropyl alcohol thermolysis experiments without the purification with EDTA, the reaction rate constant values were anomalously high and showed a poor reproducibility.

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Registry No. ACDP, 1073-91-2; PDP, 20732-35-8; CHDP, 183-84-6.

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[16] Bladon, P.; McCullough, K. J.; Morgan, A. R.; Nonhebel, D. C.; Pauson, P. L.; White, G. J. *J. Chem. Res. Synop.* **1980**, 284.

[17] McCullough, K. J.; Morgan, A. R.; Nonhebel, D. C.; Pauson, P. L.; White, C. J. *J. Chem. Res. Synop.* **1980**, *2*, 34.

[18] Cafferata, L. F. R.; Cañizo, A. I., to be published.

[19] Huyberetch, S.; Halleux, A.; Kruys, P. *Bull. Soc. Chim. Belg.* **1955**, *64*, 203.

Notes

ESR Detection and ab Initio Computation of the Two Rotational Barriers in (Aryloxy)methyl Radicals

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Alkoxymethyl radicals ($RO\dot{C}H_2$) have been reported to display restricted rotation about the O–$\dot{C}H_2$ bond.[1-5] This can be detected by ESR spectroscopy since it leads to two different hyperfine splitting constants (a_H) for the two methylenic hydrogens. In some cases, linewidth alternation at different temperatures allowed the corresponding rotational barriers to be obtained.[3,4] In particular, the free energies of activation have been measured[3] for $MeO\dot{C}H_2$ and $EtO\dot{C}H_2$ ($\Delta G^* = 5.3$ and 5.7 kcal/mol, respectively).[6]

For (aryloxy)methyl radicals ($ArO\dot{C}H_2$) the possibility of investigating this stereodynamical process is less favorable since conjugation between the Ar group and the oxygen is expected to reduce the $O\dot{C}H_2$ barrier, thus making hindered rotation more difficult to detect. Indeed, in an ESR study of the $PhO\dot{C}H_2$ radical and on some of its substituted derivatives, Hudson and Root[7] were unable to detect two different CH_2 splittings, which made it impossible to determine the activation energy for the $O\dot{C}H_2$ rotational processes. However, these authors did observe[7] a broadening of the central region of the ESR spectrum with respect to the outer wings, which indicates that a dynamic process was taking place, although its rate could not be measured. In the present work we have succeeded in measuring the $O\dot{C}H_2$ rotational barrier in $ArO\dot{C}H_2$ radicals and have found experimental evidence for a second restricted motion which is rotation about the Ar–O bond. We were encouraged to undertake these experiments as a result of the predictions of ab initio calculations on some $ArO\dot{C}H_2$ radicals, in which Ar was phenyl, furan, and

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[1] Hudson, A.; Root, K. D. J. *Tetrahedron* **1969**, *25*, 5311.

[2] Dobbs, A. J.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc. A* **1971**, 124.

[3] Biddles, I.; Hudson, A.; Wiffen, J. T. *Tetrahedron* **1972**, 867.

[4] Gaze, C.; Gilbert, B. C. *J. Chem. Soc., Perkin Trans. 1* **1977**, 126.

[5] Griller, D.; Nonhebel, D. C.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1817.

[6] The corresponding ΔH^* values, in the range where the measurements were carried out (−80, −30 °C), turned out to be 4.9 and 5.3 kcal/mol, respectively, with ΔS^* values equal to −2 eu in both cases.

[7] Hudson, A.; Root, K. D. J. *J. Chem. Soc. B* **1970**, 656.

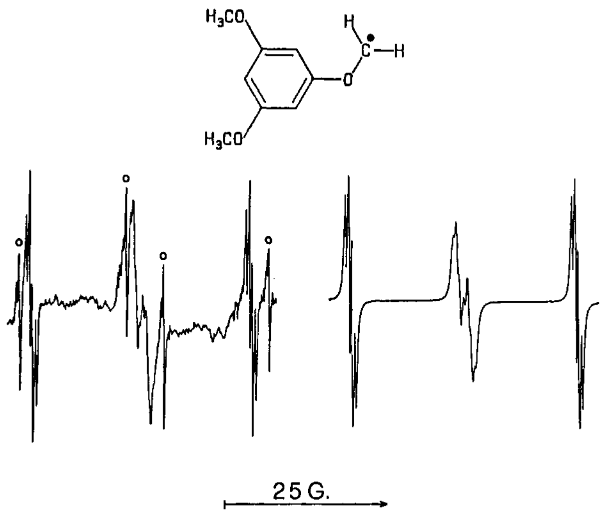


Figure 1. Experimental (left) and computer simulated (right) ESR spectra of radical **2** obtained at −122 °C in cyclopropane as solvent. The lines marked with circles are those of the cyclopropyl radical generated by H abstraction from the solvent. The simulation has been obtained with the a_H values given in the text, a rate constant of 3×10^6 s^{-1} and a line width of 0.25 G.

thiophene. The conclusions drawn from these calculations will be discussed in the present work along with the experimental evidences.

Results and Discussion

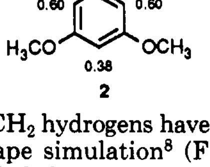
Photolysis of di-*tert*-butyl peroxide in the presence of anisole yields the radical $PhO\dot{C}H_2$ (**1**).[7] Unfortunately,

$$Me_3COOCMe_3 \xrightarrow{h\nu} 2Me_3CO^\bullet$$

$$Me_3CO^\bullet + C_6H_5OCH_3 \rightarrow Me_3COH + \underset{\mathbf{1}}{C_6H_5O\dot{C}H_2}$$

even at −130 °C (in cyclopropane as solvent) although the group of central lines in the spectrum of **1** were significantly broadened by the rotational exchange, they did not split into the two groups of signals expected for nonequivalent $O\dot{C}H_2$ hydrogens. We attributed this disappointing result to the difference between the two CH_2 splittings being insufficient with respect to the extension of the complex group of lines due to the couplings with the five ring hydrogens.

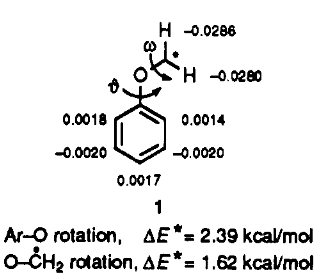
In order to simplify the spectrum and in the hope of making such a difference detectable, the experiment was repeated with the 3,5-dimethoxyanisole. This molecule was selected because it yields radical **2**, whichever methoxy group is attacked by the $Me_3CO^\bullet$ radical and because the absence of splitting by the two meta hydrogens in **1** causes **2** to have a simpler ESR spectrum. The experimental a_H splittings, in Gauss, are given below.



2

At −130 °C, the CH_2 hydrogens have different a_H values. Computer line shape simulation[8] (Figure 1) at various temperatures yielded the free energy for rotation about the $O\text{–}\dot{C}H_2$ bond: $\Delta G^* = 4.15 \pm 0.2$ kcal/mol. As would be expected, the rotation barrier in **2** is considerably lower than that measured[6] for the same process in the analogous aliphatic radicals.

Scheme I



It has also pointed out[7] that the ArO conjugation, which is responsible for the lowering of the $O\dot{C}H_2$ rotational barrier, should make the ArO rotational barrier high enough to be experimentally observable. In order to have some indication regarding the relative energy barriers involved in these two dynamic processes an ab initio theoretical investigation was carried out at the 3-21G[9,10] level for radical **1** (the computed spin densities are given in Scheme I). By optimizing the geometry[11] of the planar ground state and assuming a rigid rotation about the angles ϑ or ω (Scheme I), the barriers for the Ar–O or O–CH_2 rotations could be computed as the difference (ΔE^*) between the energy of the ground state and that of the two twisted conformations having, respectively, ϑ or ω equal to 90°.

The computed barrier for the Ar–O rotation is higher than that for the $O\text{–}\dot{C}H_2$ rotation and although the calculated barriers cannot be expected to match the experimental barriers, their relative ordering should be correct. Accordingly the Ar–O rotational barrier is expected to be higher than 4.15 kcal/mol and should therefore be observable at the temperatures where the restricted $O\text{–}\dot{C}H_2$ rotation was detected. However, the calculations also predict an exceedingly small difference between the spin densities for the two ortho positions (i.e. 0.0004). It therefore seems likely that the difference between the two ortho hydrogen splittings is less than the experimental linewidth. Indeed, even carefully resolved traces (linewidth 0.04 G at −100 °C) of the outer wings of the spectrum of **1** did not reveal the additional splittings expected nor did it display any selective line broadening.[12] Our conclusion that the barrier to Ar–O rotation is larger in $ArO\dot{C}H_2$ radicals than that for the $O\text{–}\dot{C}H_2$ rotation thus rests only on theoretical grounds. The ab initio calculations also predict an increase in the $O\text{–}\dot{C}H_2$ rotational barrier when less aromatic rings (such as, for instance, furan and thiophene) are bonded to the OCH_2 moiety. Calculations indicate that for the furyl radical (**3**) the more stable conformer (syn **3a**, $\vartheta = 0°$) has an energy 1.71 kcal/mol lower than that of the less stable conformer (anti **3b**, ϑ =

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(8) Lunazzi, L.; Placucci, G.; Grossi, L.; Guerra, M. *J. Chem. Soc., Perkin Trans. 2* **1982**, 43.

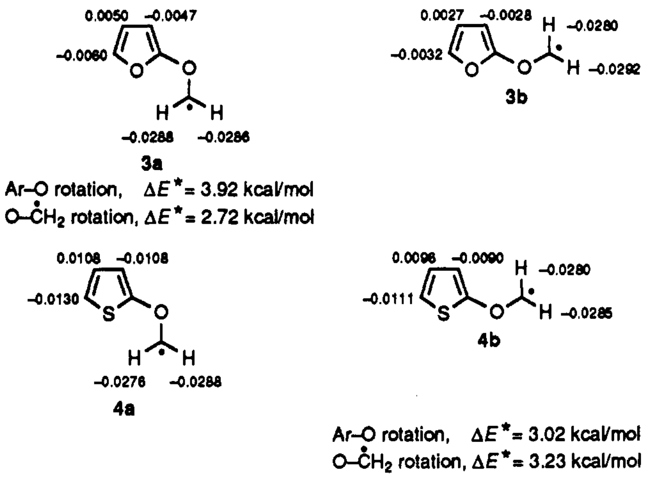
(9) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Polple, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

(10) Computation have been performed with the GAUSSIAN 82 series of programs: Binkley, J. S.; Frisch, M.; Krishian, R.; De Frees, D. J.; Schlegel, H. B.; Whitesiede, R. A.; Fluder, E.; Seeger, R.; Pople, J. A. Gaussian 82, Carnegie Mellon University, Pittsburg, PA, 1982.

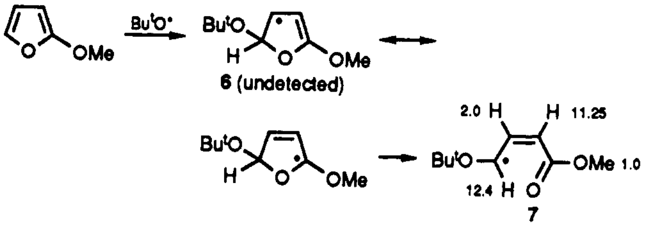
(11) In the cases reported here the geometries have been fully optimized with an analytical gradient procedure: Pulay, P. In *Applications of Electronic Structure Theory*; Schaefer, H. F. III, Ed.; Plenum Press: New York, 1977. Schlegel, H. B. *J. Chem. Phys.* **1982**, *77*, 3676.

(12) A similar behavior has been observed in the ^{13}C NMR spectra of benzoates which did not display, at low temperature, the nonequivalence of the ortho chemical shifts due to the restricted rotation: Anet, F. A. L.; Ghiaci, M. *J. Chem. Soc., Chem. Commun.* **1979**, 588. It was subsequently demonstrated that this was the result of an accidental degeneracy which could only be removed in a few selected derivatives: Lunazzi, L.; Macciantelli, D.; Spinelli, D.; Consiglio, G. *J. Org. Chem.* **1982**, *47*, 3759.

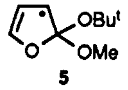
Scheme II



Scheme III



180°). In the case of thienyl radical 4 the energy difference for the two conformers (**4a** and **4b**) is computed to be 0.31 kcal/mol, the anti (**4b**) being now the more stable. The calculated spin densities and the rotational barriers are summarized in Scheme II. Unfortunately, H abstraction from the OCH_3 group of 2-methoxyfuran to yield radical 3 did not occur. Instead, the ESR spectrum of a typical allylic radical was obtained.[13-16] The a_H values (in Gauss) are 12.4 (1 H), 2.0 (1 H), 11.25 (1 H), and 1.0 (3 H). These splittings might, in principle, correspond to those of radical 5, generated by addition of t-BuO$^{\bullet}$ to the double bond of the furan. It is not clear, however, why t-BuO$^{\bullet}$ should add



5

at the 2-position, which already bears the OMe group, rather than at the less hindered 5-position. Furthermore the measured g factor (2.0040) is inconsistent with those of analogous allylic radicals obtained by addition of RO$^{\bullet}$ radicals to furan (2.0026–2.0031).[13] We therefore suggest that the allylic radical we observe is 7, a radical which could be obtained via the reaction sequence shown in Scheme III. That is, addition occurs at the more favored[17] position

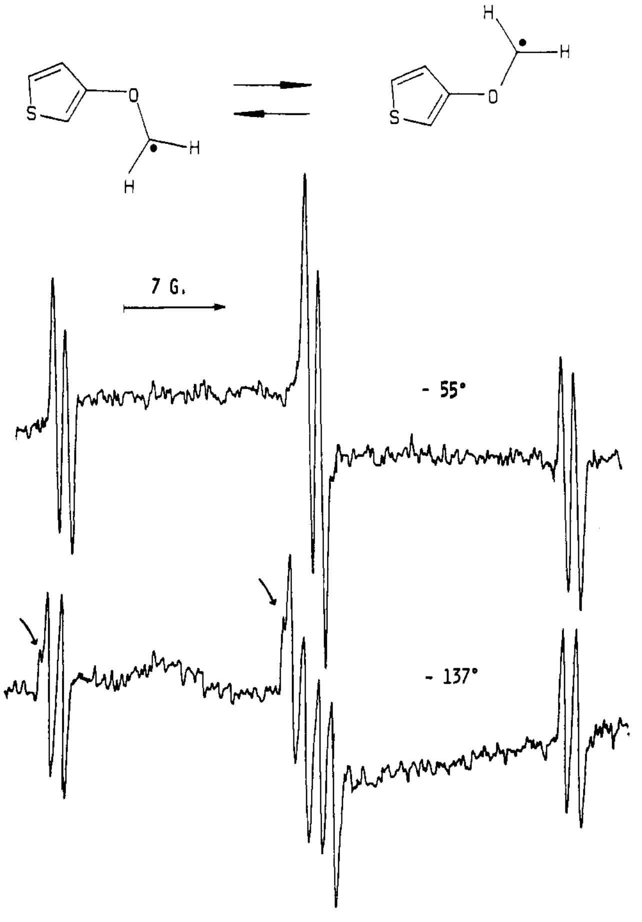


Figure 2. ESR spectrum of the radical 9 obtained by H abstraction from 3-methoxythiophene. At −55 °C the spectrum displays three pairs of lines (1:2:1 intensity ratio) due to the large (17.5 G) splitting with the two equivalent $O\dot{C}H_2$ hydrogens and to the small (0.85 G) splitting with one of the three ring hydrogens (the remaining ring splittings being zero). On lowering the temperature (−137 °C) the central doublet splits into four lines owing to the nonequivalence of the $O\dot{C}H_2$ hydrogens due to the restricted $O-\dot{C}H_2$ rotation. Two additional lines (indicated by the arrows) were also detected: they coalesce reversibly with their more intense companions and were thus believed to be the visible part of the spectrum of the less stable conformer generated by the restricted Ar–O rotation (see text). The linewidth of both spectra is about 0.35 G.

5 and is followed by the opening of the furan ring. Radicals of this type have been reported,[18] and their hydrogen hyperfine splittings, as well as their g factors, are in general agreement with the present values.

In the case of 2-methoxythiophene, both H abstraction from OCH_3 and t-BuO$^{\bullet}$ addition to the thiophene ring occur simultaneously, yielding two different radicals. The complexity of the resulting superimposed ESR spectra, accompanied by a poor signal to noise ratio, prevented both a spectral analysis of the adduct radical and a temperature-dependent line shape study[19] of the abstraction radical 4. Nonetheless, the averaged a_H splittings for radical 4

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(13) Lunazzi, L.; Placucci, G.; Grossi, L. *J. Chem. Soc., Perkin Trans. 2* **1982**, 875.

(14) Burkey, T. J.; Griller, D.; Lunazzi, L.; Nazran, A. S. *J. Org. Chem.* **1983**, *48*, 3704.

(15) Lunazzi, L.; Placucci, G.; Grossi, L. *J. Chem. Soc., Chem. Commun.* **1979**, 533.

(16) Lunazzi, L.; Placucci, G.; Grossi, L. *Tetrahedron* **1983**, *39*, 159.

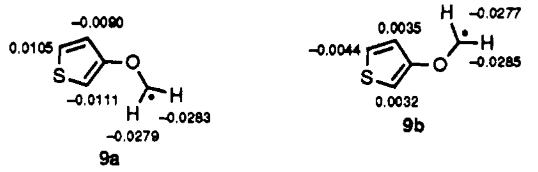
(17) Support for the fact that addition of the t-BuO$^{\bullet}$ is unlikely to occur at position 2 comes from the ESR spectrum of radical 8, obtained by reaction of t-BuO$^{\bullet}$ with 2-(methylthio)furan. The presence of the SMe group inhibits, apparently, the ring opening, and the ESR spectrum thus corresponds to that of a radical analogous to 6 where the OMe is replaced by the SMe group. The hyperfine splittings (in Gauss) are as follows: 25.9 (1 H), 12.1 (1 H), 1.75 (1 H). The 25.9-G splitting (which was not present in 7) is actually typical of an hydrogen bonded to a sp^3 carbon adjacent to the allylic cyclic moiety.[13] The absence of one of the two large allylic splittings in the spectrum of 8 is consistent with the absence of one of the hydrogens of the allylic moiety which has been replaced by the SMe group.

(18) Dixon, W. T.; Foxall, J.; Williams, G. H.; Edge, D. J.; Gilbert, B. C.; Kazarians-Moghaddam, H.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1977**, 827. Sustmann, R.; Trill, H.; Brandes, D. *Chem. Ber.* **1977**, *110*, 245.

(19) Attempts to increase the preference for H abstraction by using the 2,5-dimethoxythiophene failed in that no ESR spectrum at all was detected.

(20) Also in the case of a radical anion containing the thiophene ring the minor rotational conformer displayed only three lines differing from those of the major conformer, owing to the closeness of the two sets of hydrogen splittings: Lunazzi, L.; Mangini, A.; Placucci, G.; Spagnolo, P.; Tiecco, M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 19.

Scheme IV



Ar–O rotation, $\Delta E^* = 3.75$ kcal/mol
O–$\dot{C}H_2$ rotation, $\Delta E^* = 2.94$ kcal/mol

could be disentangled and are as follows: 0.8 G (2 H), 17.6 G (2 H). The small splitting corresponds to a pair of accidentally equivalent positions in the ring (the third ring splitting being 0) and the large splitting to the pair of OCH_2 hydrogens.

Finally, radical **9** could be obtained from 3-methoxythiophene. Its ESR spectrum at −40 °C is even simpler than that of **2** in that it features a triplet (a_H = 17.5 G) for the pair of the CH_2 hydrogens and a doublet (a_H = 0.85 G) for one of the ring hydrogens. The ab initio calculations (Scheme IV) indicate that **9a** is more stable than **9b** by 1.8 kcal/mol: the observed ring splitting was assigned to position 2. At lower temperatures (below −120 °C) the spectrum of **9** displays two different CH_2 splittings (16.7 and 18.7 G) and this allowed us to determine, by computer line shape simulation, a value of 4.7 ± 0.2 kcal/mol for the O–$\dot{C}H_2$ rotational process. Such a value, as predicted by the calculations, is indeed larger than that determined for **2** (4.15 ± 0.2 kcal/mol). Even more interesting is the observation that in the spectrum of **9**, below −120 °C, two additional lines were also detected (Figure 2). The intensity of each of these lines is about 20–30% that of each line of the main spectrum, and they coalesce in a reversible manner with the corresponding more intense companions. These less intense lines are most likely due to the second conformer, generated by the restricted rotation about the Ar–O bond: according to the ab initio calculations they are part of the spectrum of the less stable conformer **9b**. Owing to the presence of only two visible lines, a complete analysis of the spectrum of the minor conformer could not be carried out. However, the fact that the majority of the spectral lines of the two conformers are superimposed indicates that the two sets of hyperfine splittings are extremely similar. Only the existence of two different *g* factors allowed two spectra for the two conformers to be detected. This lends support to the view that, in the case of **1** and **2** (where symmetry prevents the existence of conformers and hence of different *g* factors), the difference of the H splittings for the ortho positions is too small to be detected. Furthermore, in the ESR spectrum of radical **9** the separation of the ESR lines corresponding to the pair of rotational conformers (0.5 G) is much smaller than that (2.0 G) originated by the restricted O–$\dot{C}H_2$ rotation. The latter coalesce, nonetheless, in the same temperature range of the former ones, thus indicating that the Ar–O rotational barrier of **9** (although not accurately measurable) cannot be smaller (and is most likely larger) than that of the O–$\dot{C}H_2$ barrier, in agreement with the theoretical predictions.

Conclusions

With this final experiment on 3-methoxythiophene we have obtained evidence for the existence of the restricted Ar–O rotation in radicals of the type $ArO\dot{C}H_2$. Such an effect can only rarely be observed owing to similarity of the splittings of the ring hydrogens in positions syn and anti to the CH_2 moiety. On the other hand, the a_H values of the two methylenic hydrogens are sufficiently different that accurate determinations of O–$\dot{C}H_2$ rotational barriers can be made provided appropriate compounds are selected and sufficiently low temperatures reached.

Experimental Section

Materials. 1,3,5-Trimethoxybenzene and 2-methoxyfuran were commercially available and were purified before the use. 2-Methoxythiophene,[21] 3-methoxythiophene,[22] and 2-methylthiofuran[23] were prepared following the literature. 2,5-Dimethoxythiophene was prepared[21] by refluxing for 75 h the commercially available 2,5-dibromothiophene (6 g, 25 mmol) with 2.2 g (27 mmol) of cupric oxide in a flask containing 40 mL of 10% sodium methoxide in methanol (174 mmol). The reaction mixture was cooled, the solid part was filtered off, and the solvent was removed. The residue was poured on water (50 mL) and extracted with Et_2O. After the organic layer was dried and the solvent was eliminated, the crude product was distilled at low pressure: yield 1.6 g (45%); bp (5 mmHg) 92–93 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 3.8 (6 H, s, CH_3), 5.8 (2 H, s, CH); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 60.4 (q, CH_3), 101.1 (d, CH), 154.7 (s, C). Anal. Calcd for $C_6H_8O_2S$: C, 50.0; H, 5.5. Found: C, 49.6; H, 5.8.

ESR Measurements. The spectra were obtained by photolysis of cyclopropane solutions containing di-*tert*-butyl peroxide within the cavity of an ESR spectrometer (Varian E-3). The samples were prepared by condensing the cyclopropane into quartz tubes (containing the appropriate material) connected to a vacuum line. The tubes were then sealed in vacuo. The temperatures were monitored by inserting a thermocouple in the ESR cavity before or after the spectral measurements.

Acknowledgment. We gratefully thank Prof. F. Bernardi (University of Bologna) for helpful comments and stimulating discussions on performing and interpreting the theoretical calculations. Financial support has been received from the Ministry for the Scientific Research (MURST) and from the CNR.

Registry No. **1**, 17374-79-7; **2**, 69305-47-1; **3**, 130410-19-4; **4**, 130410-20-7; **7**, 130410-21-8; **9**, 130410-22-9; $Me_3CO^\bullet$, 3141-58-0; 1,3,5-trimethoxybenzene, 621-23-8; 2-methoxyfuran, 25414-22-6; methoxythiophene, 16839-97-7; 3-methoxythiophene, 17573-92-1; 2-methylthiofuran, 13129-38-9; 2,5-dimethoxythiophene, 58386-20-2; 2,5-dibromothiophene, 3141-27-3; di-*tert*-butyl peroxide, 110-05-4.

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(21) Sicè, J. *J. Am. Chem. Soc.* **1953**, *75*, 3697.
(22) Gronowitz, S. *Arkiv. kemi* **1958**, *12*, 239.
(23) Kossuki, H.; Mory, Y.; Ohtsuka, T.; Nishizawa, H.; Ochi, M.; Matsuoka, K. *Heterocycles* **1987**, *26*, 2347.

A Useful New Enantiomerically Pure Synthon from Malic Acid: Chelation-Controlled Activation as a Route to Regioselectivity

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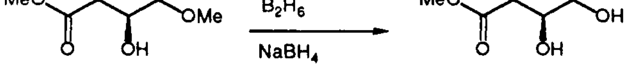
Recently, we had need of aldehyde **1**, which could, in principle, be obtained in optically active form from malic acid. However, no simple methods for achieving the required transformations are presently known. The closest report is that of Saito, who found that reduction of dimethyl malate (**2**) with diborane and catalytic amounts of



2 **3**