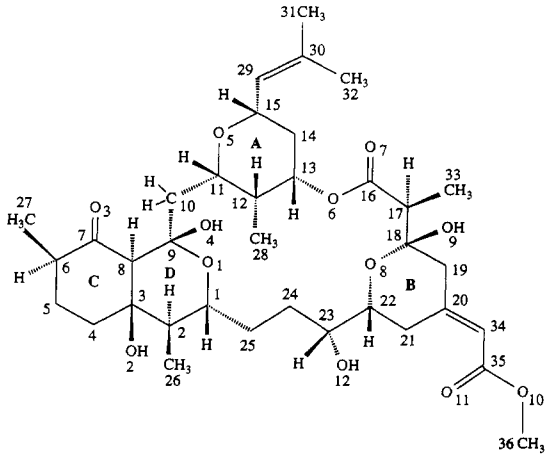

Figure 2. Numbered structure of miyakolide (**1**).

OAc/CCl_4 and measured on a Nonius CAD4 diffractometer at 220 K. It exhibited an ordered structure, from which the relative configuration of the whole molecule was determined (Figure 1).[5] The perspective drawing of **1** shows that it is a macrolide possessing three hydropyran rings, two hemiketal functionalities, and a methyl ethylidenoate substituent attached to a hydropyran ring (Figure 2). All of the 6-membered rings exist in chair conformations, while rings C and D are trans-fused. The 16-membered ring of the macrolide portion adopts a quinquangular conformation [4*4*4*4*4].[8,9]

Unlike the bryostatins, which possess potent anti-neoplastic properties, miyakolide only displayed weak in vitro (IC_{50} 17.5 μg/mL) and in vivo antitumor activity (T/C 127% at 800 μg/kg) against P388 mouse leukemia.[11] The disparity in activity may be due to subtle differences between the macrolide portions of the two molecules. Both bryostatin-1 and miyakolide are bound by outer perimeters of 26 atoms. However, the inner perimeters consist of 20 and 16 atoms, respectively. In bryostatin-1, the hydropyran rings are all cis-substituted at the 2,6-positions. Interestingly, although the corresponding 6-membered rings are similarly cis-substituted in miyakolide, one of the hydropyrans, ring A, is not incorporated as an ether link in the 16-membered macrocycle since it is joined by the C(11) and C(13) atoms (Figure 2). Consequently, miyakolide may not bind cations so well, which may possibly account for its diminished activity.

Supplementary Material Available: Tables of crystallographic data, including positional parameters, isotropic and anisotropic displacement parameters, bond distances and angles, and dihedral angles (9 pages); table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

(5) Crystallographic data for **1**: $C_{36}H_{54}O_{12}$ (C_4H_8O), M_w = 678.9/72.0, orthorhombic, $P2_12_12_1$°, a = 12.717 (3), b = 15.264 (4), c = 20.591 (4) Å, V = 3997 (2) Å^3, Z = 4, D_c = 1.25 g cm^{-3}, $F(000)$ = 1624, μ(Mo Kα) = 0.086 mm^{-1}; $R = \omega R$ = 0.081 (ω = 1) for 2414 observed reflections ($|F_o| > 4\sigma(F_o)$). The structure was solved by direct methods (Multan-87)[6] and refined by full-matrix least-squares (X-TAL).[7] All the coordinates of the H atoms were calculated, except those of the three hydroxyl groups which were determined by a difference electron density map.

(6) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data*; Universities of York and Louvain: England, and Louvain-la-Neuve, Belgium, 1987.

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(8) Bernardinelli, G.; Gerdil, R. *Helv. Chim. Acta* **1982**, *65*, 558.

(9) This notation seems to be more appropriate than that of Dale[10] on account of the presence of four strain-free anti-gauche-anti sequences in the macrocycle.

(10) Dale, J. *Acta Chem. Scand.* **1973**, *27*, 115.

(11) Other in vitro bioassay results are IC_{50} 17.1 μg/mL (A-549 human lung carcinoma cells) and >20 μg/mL (HT-29 human colon adenocarcinoma cells) and in vivo activity T/C 123% at 400 μg/kg against B-16 melanoma.

Rate of Interconversion of Syn and Anti Rotamers of $Mo(CHCMe_2Ph)(NAr)(OR)_2$ and Relative Reactivity toward 2,3-Bis(trifluoromethyl)norbornadiene

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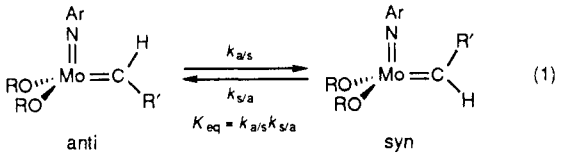
Received May 5, 1992

Alkylidene complexes of the type $M(CHR')(NAr)(OR)_2$ (M = Mo or W; R' = alkyl, aryl, etc.; Ar = 2,6-C_6H_3-*i*-Pr_2) are useful initiators for the polymerization of cyclic olefins,[1-6] in some cases in a living manner[1] and stereoselectively.[6] Syn and anti rotamers of such species have been observed in solution when OR is a phenoxide ligand, and they have been shown to interconvert with $\Delta G^{\ddagger}$ = 16–18 kcal mol^{-1} (eq 1).[7] We have now acquired such



(1)

data for molybdenum compounds that contain OR = $OCMe_3$ (OR_{F0}), $OCMe_2(CF_3)$ (OR_{F3}), $OCMe(CF_3)_2$ (OR_{F6}), and $OC(CF_3)_2(CF_2CF_2CF_3)$ (OR_{F13}) ligands. We find that the rate of interconversion of rotamers and their reactivities can vary by many orders of magnitude, and that under at least some circumstances the rotamer that is present in vanishingly small quantities is the most reactive toward 2,3-bis(trifluoromethyl)norbornadiene.

An alkylidene H_α resonance for *anti*-$Mo(CHCMe_2Ph)(NAr)(OR)_2$ compounds (OR = OR_{F3}, OR_{F6}, or OR_{F13}) can be observed upon photolysis at 366 nm in toluene-d_8 or THF-d_8 at −80 °C for several hours. Photostationary mixtures that contain up to 35% of the anti rotamer usually are obtained after approximately 4 h of photolysis. The anti H_α resonance appears downfield of the syn H_α resonance and has a characteristic[7,8] relatively large value for $^1J_{CH\alpha}$ (140–155 Hz; see supplementary material). The H_α resonance for *anti*-$Mo(CHCMe_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$ could not be observed in similar experiments.

The first-order rate of conversion of the anti rotamer to the syn rotamer was determined by ^{1}H NMR at several appropriate temperatures versus an internal standard (25 runs; see Table V in supplementary material). (Most rate constants so far have been determined over a range of only ~15 °C, so the accuracy of some of the more extreme values found in Table I (calculated at 25 °C employing the Eyring equation) may not be high.) We find that in toluene-d_8 the rate of rotamer isomerization slows dramatically as the alkoxide ligands become more electron withdrawing, decreasing by approximately 3 orders of magnitude in the series **2**–**4**. Since *anti*-**1** could not be observed upon photolysis of *syn*-**1** (in either THF-d_8 or toluene-d_8) at −80 °C, we can only estimate that the rate of conversion of *anti*-$\mathbf{1}_{tol}$ to *syn*-$\mathbf{1}_{tol}$ is probably at least 2 orders of magnitude faster than that of *anti*-$\mathbf{2}_{tol}$ to *syn*-$\mathbf{2}_{tol}$. Therefore the rate of conversion of anti to syn rotamer decreases approximately 5 orders of magnitude in the series $\mathbf{1}_{tol}$–$\mathbf{4}_{tol}$.

The H_α resonance in the anti rotamer could be located at room temperature (for OR_{F3}, OR_{F6}, and OR_{F13}) or 0 °C (for OR =

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(3) Bazan, G. C.; Oskam, J. H.; Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899.
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(5) Wu, Z.; Wheeler, D. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 146.
(6) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.
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Table I. Rates of Interconversion and Equilibrium Constants at 25 °C for Syn and Anti Rotamers of $Mo(CHCMe_2Ph)(NAr)(OR)_2$[a]

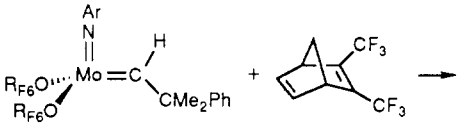
cat.,solv	OR	$k_{a/s}$ (s^{-1})	$K_{eq}(298)$	$k_{s/a}$ (s^{-1})	$\Delta G°_{298}$[b]
$\mathbf{1}_{tol}$	OR_{F0}	~1000[c]	1200[d]	~1	−4.2
$\mathbf{2}_{tol}$[e]	OR_{F3}	6.6	1850	4×10^{-3}	−4.5
$\mathbf{3}_{tol}$	OR_{F6}	0.07	1450	5×10^{-5}	−4.3
$\mathbf{4}_{tol}$	OR_{F13}	4.2×10^{-3}	620	7×10^{-6}	−3.8
$\mathbf{2}_{thf}$	OR_{F3}	0.24	1400	2×10^{-4}	−4.3
$\mathbf{3}_{thf}$	OR_{F6}	4.4×10^{-5}	23	2×10^{-6}	−1.9

[a] See supplementary material for activation parameters from which $k_{a/s}$ values are calculated at 298 K using the Eyring equation. [b] kcal mol^{-1}. [c] Estimated assuming that T_c is 25 °C and that $\nu_{anti} - \nu_{syn} \approx 400$ Hz. [d] K_{eq} was measured at 0 °C, since the anti rotamer interconverts rapidly with the syn rotamer at 25 °C on the NMR time scale. [e] For the analogous $CHCMe_3$ complex, $k_{a/s} = 10.5$, $K_{eq} = 2200$, $k_{s/a} = 5 \times 10^{-3}$, and $\Delta G°_{298} = -4.6$.

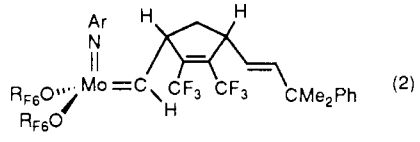
$OCMe_3$) at 500 MHz and integrated versus the downfield ^{13}C satellite of the syn H_α resonance. Therefore we could determine K_{eq}, $\Delta G°$, and $k_{s/a}$, the rate constant for conversion of syn to anti (Table I). K_{eq} is relatively constant in the series $\mathbf{1}_{tol}$–$\mathbf{4}_{tol}$, the difference in standard free energy between anti and syn rotamers being approximately 4 kcal mol^{-1}. Since K_{eq} is relatively constant, $k_{s/a}$ also varies approximately 5 orders of magnitude in the series $\mathbf{1}_{tol}$–$\mathbf{4}_{tol}$.

Similar experiments were carried out in THF-d_8 for two complexes ($\mathbf{2}_{thf}$ and $\mathbf{3}_{thf}$ in Table I). (The nature of the THF-d_8 adducts that are likely to be present under such circumstances has not been established.) Both $k_{a/s}$ and $k_{s/a}$ decrease approximately 1 order of magnitude for $\mathbf{2}_{thf}$ versus $\mathbf{2}_{tol}$, but $k_{a/s}$ decreases approximately 3 orders of magnitude for $\mathbf{3}_{thf}$ versus $\mathbf{3}_{tol}$. These findings are consistent with the expected stronger binding of THF-d_8 to a more electrophilic metal, along with the fact that a coordinating ligand must be lost from a five-coordinate species in order for rotamers to interconvert.[7]

The relative reactivities of syn and anti rotamers with 2,3-bis(trifluoromethyl)norbornadiene ($NBDF_6$) have been determined qualitatively when OR = $OCMe(CF_3)_2$ by adding $NBDF_6$ to the mixture of syn and anti rotamers generated by photolysis at −80 °C. A toluene-d_8 sample containing 33% *anti*-**3** was frozen at 77 K, 5 equiv of $NBDF_6$ was added, and the sample was thawed and rapidly transferred to a −80 °C NMR probe. The H_α resonance for the anti rotamer had been replaced by an H_α resonance for the syn "first insertion product" (*syn*-$\mathbf{3}(+1)_{tol}$; $^3J_{H\alpha H\beta} = 8.1$ Hz) downfield from the H_α resonance for unreacted *syn*-$\mathbf{3}_{tol}$ (eq 2; see also below and Figure 1). The C=C double bond in



anti-**3**



(2)

syn-**3**(+1)

syn-$\mathbf{3}(+1)_{tol}$ was found to be trans ($^3J_{HH} = 15.4$ Hz). After 1 h at −40 °C, all monomer was consumed by *syn*-$\mathbf{3}_{tol}$ and *syn*-$\mathbf{3}(+1)_{tol}$ to give other "living alkylidenes" (*syn*-$\mathbf{3}(+n)_{tol}$), but some *syn*-$\mathbf{3}_{tol}$ remained. Addition of only 0.33 equiv of $NBDF_6$ to a similar photolyzed mixture of *syn*-$\mathbf{3}_{tol}$ and *anti*-$\mathbf{3}_{tol}$ resulted in complete consumption of *anti*-$\mathbf{3}_{tol}$. We conclude that the reactivity of *anti*-$\mathbf{3}_{tol}$ is very much greater than that of the *syn*-$\mathbf{3}_{tol}$ and estimate that difference to be at least 2 orders of magnitude. We also can conclude that *only a trans C=C bond is formed when $NBDF_6$ reacts with anti-$\mathbf{3}_{tol}$*. Finally, the mixture of 0.67 equiv of *syn*-$\mathbf{3}_{tol}$ and 0.33 equiv of *syn*-$\mathbf{3}(+1)_{tol}$ was photolyzed to give a mixture that contains *anti*-$\mathbf{3}_{tol}$ and *anti*-$\mathbf{3}(+1)_{tol}$ ($^3J_{H\alpha H\beta} = 12.4$ Hz; see also Figure 1). The rate of conversion of *anti*-$\mathbf{3}(+1)_{tol}$ to *syn*-$\mathbf{3}(+1)_{tol}$ at 0 °C could then be determined and was found to be 15 times slower than the rate of conversion of *anti*-$\mathbf{3}_{tol}$ to *syn*-$\mathbf{3}_{tol}$ at 0 °C.

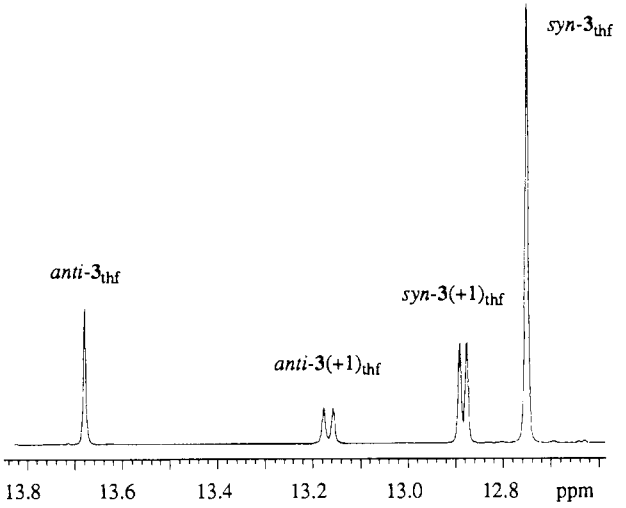


Figure 1. 500-MHz ^1H NMR spectrum at 35 °C showing the alkylidene region after the addition of 0.33 equiv of 2,3-bis(trifluoromethyl)norbornadiene to photolyzed **3** in thf-d_8, followed by further photolysis at low temperature (**3**(+1) is the "first insertion product").

Analogous experiments in THF-d_8 showed that both *anti*-$\mathbf{3}_{thf}$ and *syn*-$\mathbf{3}_{thf}$ react significantly more slowly with $NBDF_6$ than *anti*-$\mathbf{3}_{tol}$ and *syn*-$\mathbf{3}_{tol}$, respectively, as one would expect if THF-d_8 binds to the metal, but the difference in reactivity between *anti*-$\mathbf{3}_{thf}$ and *syn*-$\mathbf{3}_{thf}$ is still marked. *anti*-$\mathbf{3}_{thf}$ was consumed in a few minutes at −30 °C to again produce a syn first insertion product ($^1J_{CH} = 127$ Hz; $^3J_{H\alpha H\beta} = 7.0$ Hz) whose C=C bond is trans ($^3J_{HH} = 16$ Hz). Addition of 0.33 equiv of $NBDF_6$ to the mixture containing 0.33 equiv of *anti*-$\mathbf{3}_{thf}$ at −30 °C generated 0.33 equiv of *syn*-$\mathbf{3}(+1)_{thf}$. Subsequent photolysis of this mixture then yielded a mixture of *anti*- and *syn*-$\mathbf{3}_{thf}$, *anti*-$\mathbf{3}(+1)_{thf}$($^1J_{CH\alpha} = 152$ Hz; $^3J_{H\alpha H\beta} = 10.0$ Hz), and *syn*-$\mathbf{3}(+1)_{thf}$ (Figure 1). The rate of conversion of *anti*-$\mathbf{3}(+1)_{thf}$ to *syn*-$\mathbf{3}(+1)_{thf}$ was found to be approximately 5 times slower than the rate of conversion of *anti*-$\mathbf{3}_{thf}$ to *syn*-$\mathbf{3}_{thf}$ at 35 °C. *syn*-$\mathbf{3}_{thf}$ reacted only very slowly at 0 °C to give *syn*-$\mathbf{3}(+1)_{thf}$, *which contains a cis C=C bond*, and further insertion products (*syn*-$\mathbf{3}(+n)_{thf}$).

Additional studies will be required before we can determine the full implications of observations of the type outlined here. However, even at this stage it is clear that the polymerization pathway could depend dramatically upon conditions, the nature of the alkoxide, and the inherent reactivity of the monomer, and that reactions could proceed entirely via the minor, virtually unobservable anti rotamer if syn/anti interconversion is fast relative to the rate of polymerization, or entirely via the major syn rotamer if syn/anti interconversion is slow relative to the rate of polymerization. It is interesting to note that polymer prepared from $NBDF_6$ and $Mo(CHCMe_3)(NAr)(O\text{-}t\text{-}Bu)_2$ in toluene[6] is highly trans, while that prepared from $Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$ in THF is entirely cis,[9] consistent with such a proposal. Studies designed to correlate observations of the type outlined here with the cis/trans ratio and tacticity are under way, as are experiments designed to test whether the selectivities observed here extend to metathesis reactions involving acyclic internal olefins in some circumstances.

Acknowledgment. R.R.S. thanks the Office of Naval Research for supporting this research; Prof. James Feast and Dr. Vernon Gibson for communication of unpublished results; Dr. R. Toreki for suggesting photolysis as a means of converting syn to anti, a technique that was first employed for interconverting syn and anti

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(10) Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 3367.

rhenium alkylidene complexes;[10] and Harold H. Fox for the synthesis of $Mo(CHCMe_2Ph)(NAr)[OC(CF_3)_2CF_2CF_2CF_3]_2$.

Supplementary Material Available: NMR data, details of the kinetic studies (25 experiments), individual rate constants, and values for $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ for various interconversions (4 pages). Ordering information is given on any current masthead page.

Intramolecular Hydrogen Abstraction by Functionalized Arylcarbenes

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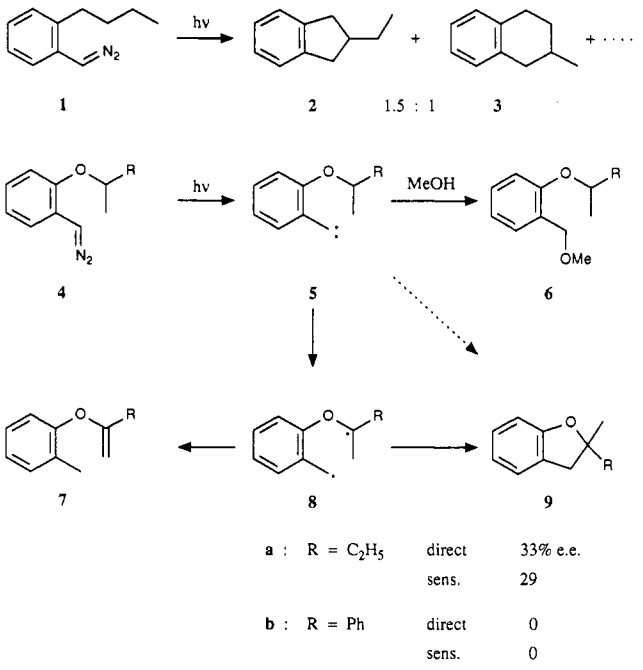
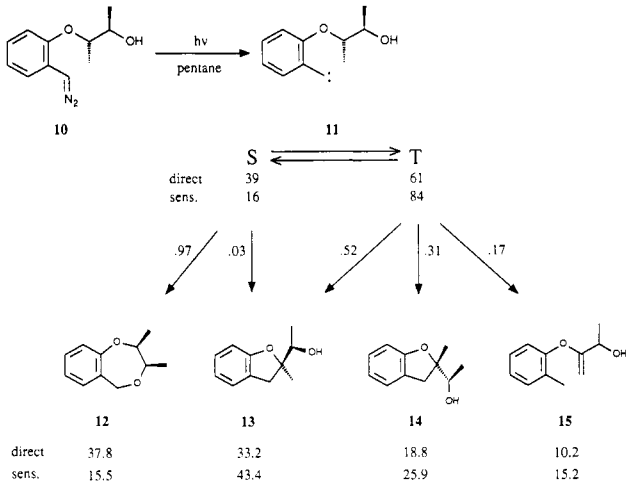
Many reactions of phenylcarbene proceed from the singlet state, although the ground state is the triplet.[1] These results have been interpreted in terms of rapid singlet–triplet equilibration, with the singlet being much more reactive than the triplet state. The concerted singlet mechanism for *intermolecular* C–H insertion reactions of phenylcarbene is supported by the lack of crossover products,[2] small deuterium isotope effects,[2] and stereoselective insertion into the tertiary C–H bonds of *rac*- and *meso*-2,3-dimethoxybutane.[3] We now report contrasting evidence for *intramolecular* C–H insertion reactions. We have found that (2-alkoxyphenyl)carbenes produce five-membered rings by way of a triplet abstraction–recombination mechanism.[4]

The intramolecular insertion of arylcarbenes into C–H bonds of an ortho side chain was pioneered by Gutsche in a study of (2-butylphenyl)carbene.[5] Photolysis of the diazo compound **1** afforded five- and six-membered rings as the major products (**2**:**3** = 1.5), both of which were thought to originate from the singlet carbene (Scheme I). The oxygen of (2-alkoxyphenyl)carbenes (**5**) exerts a strong directive effect, leading to almost exclusive formation of 2,3-dihydrobenzofurans (**9**).[6] The chirality of **9** (R ≠ CH_3) prompted us to examine the stereochemistry of the insertion reactions, **5** → **9**. Direct photolysis of optically active [2-[(1-methylpropyl)oxy]phenyl]diazomethane (**4a**) in pentane afforded **9a** with 33% ee.[7] Sensitization with benzophenone lowered the ee of **9a** slightly, to 29%. The loss of enantiomeric purity points to hydrogen abstraction by triplet **5a**, giving the diradical **8a**. The intervention of **8a** also accounts for the formation of **7a** (10%, relative to **9a**) by transfer of a second hydrogen atom (disproportionation).

Scheme I



Scheme II



When the *sec*-butyl group of **4a** was replaced with (*R*)-1-phenylethyl (**4b**), the racemic dihydrofuran **9b** and enhanced quantities of **7b** were formed (**9b**:**7b** = 3.5). The ethers **6a,b**, arising by intermolecular O–H insertion of singlet **5a,b**, were the major products obtained from direct photolyses of **4a,b** in methanol (**6a**:**9a** = 12.5; **6b**:**9b** = 17.5). On sensitization with 0.2 M benzophenone, the product ratios changed in favor of **9** (**6a**:**9a** = 2.2; **6b**:**9b** = 1.3). These data indicate that singlet **5** is quenched by methanol in preference to spin inversion ($k_S > k_{ST}$) while the intramolecular abstraction of hydrogen by triplet **5** is competitive with intersystem crossing ($k_T \cong k_{TS}$).

Residual optical activity, as observed in the case of **9a**, may be due to a minor contribution of singlet **5a**. On the other hand, stereoselective ring closure of the diradical **8a** can take place if the rates of rotation and spin inversion are of similar magnitude. In order to differentiate between these alternatives, we utilized hydroxyl groups as internal traps for the singlet carbene. The (*R**,*S**)-2-hydroxy-1-methylpropyl substrate **10** and the (*R**,*R**) diastereomer (not shown) were prepared from *cis*- and *trans*-2,3-dimethyloxirane, respectively, with an appropriate phenoxide.

(1) For reviews, see: (a) Platz, M. S.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum Press: New York, 1990; Chapter 8. (b) Wentrup, C. In *Carbene(oide), Carbine, Houben-Weyl* E 19b; Regitz, M., Ed.; Thieme: Stuttgart, 1989; p 824. (c) Schuster, G. B. *Adv. Phys. Org. Chem.* **1986**, *22*, 311. (d) Moss, R. A., Jones, M., Jr., Eds. *Carbenes*; Wiley: New York, 1973, 1975; Vols. I and II. (e) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; Chapter 7.

(2) Savino, T. G.; Kanakarajan, K.; Platz, M. S. *J. Org. Chem.* **1986**, *51*, 1305. Analogous data have been reported for 1-naphthylcarbene: Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928.

(3) Kirmse, W.; Staubach, B. Unpublished results. The ratio of diastereomeric insertion products was 98.5:1.5 for *rac*-2,3-dimethoxybutane and 3.5:96.5 for *meso*-2,3-dimethoxybutane.

(4) A similar mechanistic dichotomy has been noted for intramolecular and intermolecular addition reactions of arylcarbenes to C=C bonds: (a) Kirmse, W.; Hömberger, G. *J. Am. Chem. Soc.* **1991**, *113*, 3925. (b) Hömberger, G.; Dorigo, A. E.; Kirmse, W.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 475.

(5) (a) Baer, T.; Gutsche, C. D. *J. Am. Chem. Soc.* **1971**, *93*, 5180. (b) Gutsche, C. D.; Bachman, G. L.; Coffey, R. S. *Tetrahedron* **1962**, *18*, 617.

(6) Crow, W. D.; Mc Nab, H. *Aust. J. Chem.* **1979**, *32*, 111. These authors generated [2-(*n*-alkoxy)phenyl]carbenes by thermolysis of tosylhydrazone sodium salts.

(7) Precursors of **4a** (72% ee) and **4b** (67% ee) were prepared from salicylaldehyde with optically active 2-butyl tosylate and 1-phenylethyl chloride, respectively. The ee of 2-[(1′-methylpropyl)oxy]benzaldehyde was determined by ^1H NMR (400 MHz) of the acetal formed with (*R*)-(+)-dimethyl tartrate. The enantiomers of 2-(1′-phenylethoxy)benzaldehyde were resolved by GC on 30-m capillary columns coated with heptakis(3-*O*-acetyl-2,6-di-*O*-methyl)-β-cyclodextrin in OV 1701. The aldehydes were converted into diazo compounds by way of the tosylhydrazones. The combined yield of **7** and **9** was 30–35%. Insertion reactions with the solvent and azine formation account for 65–70% of the substrate. The enantiomers of **9a,b** were analyzed by GC on the chiral phase indicated above. Results are corrected to 100% ee of the substrates. Experimental details are given in the doctoral thesis of I. S. Özkir, University of Bochum, 1991.

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