of catalyst (10.3% compared with 4.2%) is consistent with Ni^{II} playing a role in activation of Cl_2O. However, the inefficiency of this pathway for epoxidation must be attributed to rapid competing chlorination of the alkene and the lack of ClO^- for a ligand-exchange reaction (Figure 2).

A second mechanistic possibility would involve formation of a Ni^{III}–oxo radical through either direct reaction with HOCl (eq 1) or proton-assisted cleavage of the O–Cl bond in an association complex (eq 2).[14] The species $LNi^{III}–O^{\bullet}$ could be responsible

$$LNi^{II} + HOCl \rightarrow [LNi^{-}–OH]^+ + Cl^- \rightarrow LNi^{III}–O^{\bullet} + H^+ \quad (1)$$

$$LNi^{II} + ClO^- + H^+ \rightarrow LNi^{II}–O–Cl\cdots H^+ \rightarrow LNi^{III}–O^{\bullet} + HCl \quad (2)$$

for both H atom abstraction pathways and epoxidation. Experiments are in progress to distinguish between these pathways.

These findings are significant for two reasons. First, they demonstrate that very high turnover rates can be achieved for alkene epoxidation without resorting to elaborate catalysts[15] and exotic terminal oxidants. Second, they suggest the intermediacy of a high-valent nickel–oxygen species, either Ni^{III}–OCl or $Ni^{III}–O^{\bullet}$, whose formation is dependent upon the nature of the ligand field[16] and lability of the oxygen atom donor. Alkene epoxidation occurs under conditions implicating radical character at an alkene carbon whose properties may be harnessed for reaction with other inter- or intramolecular trapping agents.

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(14) (a) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7834–7836. (b) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8443–8452.

(15) Futhermore, more than 50% of the Ni(salen) survives the reaction if NaOCl is not used in large excess.

(16) For example, Ni^{II}(TPP) shows low turnover as an epoxidation catalyst, while 13- to 14-membered-ring square-planar complexes are generally active.[4]

Effect of 2,2-Dimethyl Substitution on the Lifetimes of Cyclic Hydrocarbon Triplet 1,3-Biradicals

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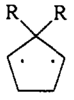
Oxygen trapping experiments have indicated that the lifetime of triplet 1,3-cyclopentanediyl (**1a**) is reduced by at least 2 orders of magnitude upon 2,2-dimethyl substitution (**1b**).[1,2] However, a question has been raised concerning the validity of the upper limit for the lifetime of biradical **1b** obtained by this method.[3] We now present direct kinetic evidence for a marked reduction of 1,3-biradical lifetimes arising from 2,2-dimethyl substitution. The presence of the benzyl chromophore in 1,3-diphenyl-1,3-cyclopentanediyl (**2a**) allowed a direct determination of its triplet lifetime by means of time-resolved flash photolysis.[4] Therefore, we chose to investigate the biradical 2,2-dimethyl-1,3-diphenyl-1,3-cyclopentanediyl (**2b**) for comparison.

Table I. Zero-Field Parameters (EPA, 77 K), Lifetimes, and Activation Parameters of the Triplet Biradicals **2** and **5**

	ESR		decay kinetics in acetonitrile[a]		
	$\lvert D/hc \rvert$, cm^{-1}	$\lvert E/hc \rvert$, cm^{-1}	$^3\tau$ (ca. 20 °C), μs	E_a, kcal/mol	log (A/s^{-1})
2a	0.047	≤0.001	16 ± 2[b]	2.6 ± 0.2[c]	6.7 ± 0.1[c]
2b	0.049	≤0.001	1.3 ± 0.1	1.2 ± 0.1[d]	6.9 ± 0.1[d]
5a	0.026[e]	≤0.002[e]	>20 000	5.3 ± 1.0[e]	5.1 ± 1.0[e]
5b	0.033[f]	≤0.002[f]	400[f]	6.8 ± 1.6[f]	8.4 ± 0.2[f]

[a] Errors are standard deviations (30 data points). [b] Instrumental settings were carefully optimized; the value of 27 μs reported previously[4] appears to contain systematic error arising from instability of the pulsed monitoring light source. [c] Temperature range 0–50 °C. [d] Temperature range −45 to 21 °C. [e] Temperature range 120–140 K, ref 11. [f] Temperature range 240–273 K, ref 12.



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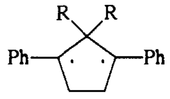

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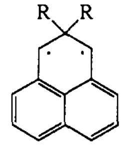

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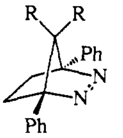

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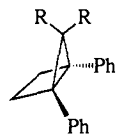

4

a: R = H

b: R = CH_3

7,7-Dimethyl-1,4-diphenyl-2,3-diazabicyclo[2.2.1]hept-2-ene (**3b**) was prepared by the usual triazoline route[5] starting from 5,5-dimethyl-1,4-diphenylcyclopentadiene. The latter was conveniently obtained[6,7] via pyrolysis of the mixture of isomeric azoalkanes resulting from the cycloaddition of norbornadiene and 4,4-dimethyl-3,5-diphenylisopyrazole. In contrast to **3a**,[4,8] the azoalkane **3b** was thermally stable for at least several days at room temperature. Direct laser photolysis of **3b** at 351 nm gave 5,5-dimethyl-1,4-diphenylbicyclo[2.1.0]pentane (**4b**) as the only product. The housane **4b** was much more stable against autoxidation than parent **4a**.[9]

Direct photolysis of **3a** and **3b** in an EPA glass (5 parts ether, 5 parts isopentane, 2 parts alcohol) at 77 K gave the triplet biradicals **2a**[8] and **2b**, respectively, which were characterized by their ESR (Table I) and fluorescence excitation and emission spectra. Both **2a** and **2b** exhibited weak, structured absorption in the visible region (ca. 460 nm) and medium-intensity absorption at ca. 320 nm (relative intensity ca. 1:40). The structured fluorescence emission showed two prominent peaks at 470 and 505 nm. The fluorescence lifetimes were determined as 217 ± 8 ns (**2a**) and 168 ± 2 ns (**2b**) by excitation with 20-ns pulses from a Nd (265 nm) or a XeF excimer laser (351 nm). The fluorescence spectra and lifetimes of both biradicals are thus similar to those of related benzyl monoradicals.[10]

The lifetime of triplet **2b** in degassed solution at ambient temperature was measured by flash photolysis using a XeF excimer laser (351 nm, 75 mJ, 20 ns) for excitation. As with **3a**,[4] no

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(1) Adam, W.; Günther, E.; Hössel, P.; Platsch, H.; Wilson, R. M. *Tetrahedron Lett.* **1987**, *28*, 4407.

(2) Adam, W.; Hössel, P.; Hümmer, W.; Platsch, H.; Wilson, R. M. *J. Am. Chem. Soc.* **1987**, *109*, 7570.

(3) The absence of oxygen trapping might be attributed to a low trapping factor[1] rather than to a short lifetime of biradical **1b**: Caldwell, R. A., personal communication.

(4) Adam, W.; Grabowski, S.; Platsch, H.; Hannemann, K.; Wirz, J.; Wilson, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 751.

(5) Adam, W.; DeLucchi, O. *Angew. Chem.* **1980**, *92*, 815; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762.

(6) Beck, K.; Höhn, A.; Hünig, S.; Prokschy, F. *Chem. Ber.* **1984**, *117*, 517. Paquette, L. A.; Leichter, L. M. *J. Org. Chem.* **1974**, *39*, 461.

(7) We thank Prof. F. G. Klärner, Bochum, for performing the high-pressure cycloaddition reaction of norbornadiene with isopyrazole.

(8) Coms, F. D.; Dougherty, D. A. *Tetrahedron Lett.* **1988**, *29*, 3753.

(9) Adam, W.; Platsch, H.; Wirz, J. *J. Am. Chem. Soc.* **1989**, *111*, 6896.

(10) Huggenberger, C.; Fischer, H. *Helv. Chim. Acta* **1981**, *64*, 338. Bromberg, A.; Meisel, D. *J. Phys. Chem.* **1985**, *89*, 2507.

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transient absorption was observed upon direct excitation of the azoalkane **3b**. At azoalkane and benzophenone concentrations of (3.1–6.5) × 10^{-3} and (1.9–3.8) × 10^{-3} M, more than 90% of the 351-nm radiation was absorbed by benzophenone. Triplet benzophenone (λ_{max} = 530 nm) was rapidly quenched by energy transfer to the azoalkane, $k_{et} = (2.5 \pm 0.2) \times 10^9$ M^{-1} s^{-1}. Biphasic decay curves, which fitted well to a dual exponential function, were observed at 320 nm, and the faster decay rate was equal to that of triplet benzophenone. The slower component of 1 μs is attributed to the decay of triplet **2b**, the lifetime of **2b** being 1 order of magnitude less than that of parent **2a** (Table I). The decay rates of the triplet biradicals **2a** and **2b** at various temperatures gave linear Arrhenius plots from which the activation parameters E_a and A were calculated (Table I).

Another example for the effect of dimethyl substitution on the lifetime of triplet biradicals is available from two separate studies of the perinaphthadiyls **5a** and **5b**,[11,12] which have so far not been considered from this perspective. Fisher and Michl[11] have determined the decay rate of **5a** in solid polyethylene at 10–140 K; the linear segment of their Arrhenius plot above ~120 K extrapolates to a lifetime of ca. 25 ms at 20 °C. To check this huge extrapolation, we generated **5a** by benzophenone-sensitized flash photolysis of naphthocyclopropane in degassed acetonitrile. The observed transient absorption had a sharp peak at 338 nm, characteristic for **5a**. The decay of **5a** was dominated by second-order contributions over the first two half-lives (first $t_{1/2} \approx$ 10 ms), which shows that the intrinsic (first-order) lifetime must be considerably longer (≥25 ms) under these conditions. The Arrhenius parameters for **5b** were determined in the range of −35 to 0 °C, with glycerol as a solvent to avoid second-order contributions.[12] The extrapolated lifetime of about 400 μs at 20 °C is in agreement with the first-order contribution to the decay of **5b** observed in less viscous solvents (benzene, acetonitrile). Again, the lifetime of the dimethyl derivative **5b** is at least 50-fold shorter than that of parent **5a**.

Thus the 1,3-biradicals **1**, **2**, and **5** consistently show a massive enhancement in the rate of triplet–singlet intersystem crossing (isc) resulting from the seemingly "innocuous" 2,2-dimethyl substitution. What is the reason for this remarkable effect? Structural differences between the **a**/**b** pairs, e.g., diminished delocalization of the unpaired electrons in **2b** as a result of the "buttressing" effect of the geminal methyl substituents, are unlikely to be responsible for the increase in isc rates, as the zero-field parameters D, which are a measure of the average distance between the unpaired electrons in triplets, are very similar in each pair (Table I).

The counteracting effects of through-bond and through-space coupling[13] are nearly balanced in the nonbonding orbitals of **1a**.[14] Dimethyl substitution gives rise to enhanced through-bond coupling, as is easily seen by Heilbronner's method.[15] This will increase the energy gap between the essentially nonbonding orbitals, lower the energy of the singlet state relative to the triplet ground state, and hence lower the energy barrier for isc.[16] Moreover, the increased difference between the energies of the nonbonding orbitals results in a greater weight of ionic contributions in the lowest singlet state wave function and hence leads to faster isc, as predicted by rule 2 of Salem and Rowland.[17] The first effect (reduced energy gap) is expected to lead to a decreased activation energy E_a for isc, while the second (increased spin–orbit coupling) should affect mainly the preexponential factor A in the biradical decay rates. Similar arguments should apply to the pairs **2a**/**2b** and **5a**/**5b**, although the experimental Arrhenius parameters (Table I), taken at face value, suggest that reasoning by analogy may be an oversimplification.[18]

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[11] Fisher, J. J.; Michl, J. *J. Am. Chem. Soc.* **1987**, *109*, 583.

[12] Hasler, E.; Gassmann, E.; Wirz, J. *Helv. Chim. Acta* **1985**, *68*, 777.

[13] Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

[14] Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284.

[15] Honegger, E.; Yang, Z.-z.; Heilbronner, E. *Croat. Chem. Acta* **1984**, *57*, 967.

[16] Ab initio calculations analogous to those of ref 14 on 2,2-dimethyltrimethylene (θ = 102°, an excellent model for **1b**) predict that the S–T gap drops to 0.44 kcal mol^{-1} vs 0.83 for the parent. Pranata, J.; Dougherty, D. A., unpublished results.

[17] Salem, L.; Rowland, C. *Angew. Chem.* **1972**, *84*, 86; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

[18] The activation energy E_a of **5b** is somewhat *higher* than that of **5a**, but this is overridden by a rather dramatic increase in the *A* factor. In view of the large difference in the conditions used to determine these Arrhenius parameters (Table I), we hesitate to consider these subtleties as significant. Furthermore, it should be recalled that the decay process of **5a** is a 2,1-hydrogen shift[11] and *not* ring closure as in **2a**, **2b**, and **5b**.

Selective Oxidation Reactions on Rh(111)-p(2×2)-O: The Conversion of Styrene to Acetophenone

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We report the unprecedented partial oxidation of an alkene to the corresponding methyl ketone by oxygen chemisorbed on Rh(111)-p(2×2)-O under ultrahigh vacuum conditions. We find that styrene ($C_6H_5C(H){=}CH_2$) reacts with atomic oxygen on Rh(111)-p(2×2)-O to form acetophenone ($C_6H_5C({=}O)CH_3$) during temperature-programmed reaction. To our knowledge, this is the first observation of olefin partial oxidation to form a ketone on Rh(111)-p(2×2)-O. Indeed, we have found that several alkenes are oxidized to the corresponding methyl ketones by oxygen on Rh(111)-p(2×2)-O, suggesting that this is a general process.[1]

The catalytic oxidation of alkenes is of extreme industrial importance since selective oxidation products serve as starting materials in the production of many specialty chemicals and polymers.[2] The reactions that we have discovered are unprecedented and proceed by a mechanism that is distinctly different from other oxidation systems. In particular, we find that allylic C–H bond activation does *not* control oxidation kinetics and selectivity on Rh(111)-p(2×2)-O.

All experiments were performed in an ultrahigh vacuum chamber, using crystal preparation and cleaning methods described in detail previously.[3] Temperature-programmed reaction data for multiple masses were obtained by using a computer-controlled UTI 100-C quadrupole mass spectrometer. The Rh(111)-p(2×2)-O surface was prepared by exposure of the initially clean Rh(111) to 1 × 10^{-8} Torr of dioxygen for 2 min at 300 K. A sharp (2 × 2) low-energy electron diffraction (LEED) pattern was observed after this procedure, and a single O(1s) peak with a binding energy of 529.5 eV was observed in the X-ray photoelectron spectrum. Styrene (99%) and styrene-d_8 (98% D) were obtained from Aldrich, dried by using CaH_2, and used without further purification.

Gaseous acetophenone is evolved in a peak centered at 275 K, with a small tail extending to 370 K, during temperature-programmed reaction of styrene on Rh(111)-p(2×2)-O (Figure 1). The selectivity for acetophenone evolution is estimated to be ~40%, based on a comparison of the integrated C(1s) X-ray photoelectron intensity at 250 K and 350 K. Similarly, the yield of acetophenone is estimated to be 0.025 molecules/Rh atom by using these data and the integrated O(1s) intensity of the (2×2)-O

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[1] Xu, X.; Friend, C. M. In preparation.

[2] See, for example: Pasquon, I. *Catal. Today* **1987**, *1*, 297.

[3] Xu, X.; Friend, C. M. *J. Phys. Chem.* **1989**, *93*, 8072–8080.

0002-7863/90/1512-4571$02.50/0