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Characterization, via ESR Spectroscopy, of Radical Intermediates in the Photooxidation of Arylcarbinols by Ceric Ammonium Nitrate

Loris Grossi* and Samantha Strazzari[1]

Dipartimento di Chimica Organica "A. Mangini", Università di Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy

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The photooxidation by ceric ammonium nitrate (CAN) of several aryl and naphthylcarbinols has been studied by means of ESR spectroscopy. For all the investigated arylcarbinols, but not for the naphthyl derivatives, it has been possible to detect radical intermediates deriving from the parent alkoxyl radicals. In particular, in the photooxidation of 1,1-diphenylethanol, a bridged-radical intermediate has been detected. The assignment has been validated through experiments with two different labeled compounds: the 1,1-[2′, 3′, 4′, 5′, 6′, 2″, 3″, 4″, 5″, 6″-$^2H_{10}$]diphenylethanol and the 1,1-diphenyl[2, 2, 2-$^2H_3$]ethanol. A similar bridged radical has been found to be formed in the photooxidation of triphenylmethanol, while, for the 1,1-diphenylpropanol, the only detectable species has been the ethyl radical deriving from a competitive β-scission process. Finally, for the 2-phenylpropan-2-ol (cumyl alcohol), two radical species have been identified: the methyl, deriving from the β-scission process, and the cyanomethylene, deriving from H-abstraction of the cumyloxyl radical from the solvent. A kinetic study on the competition of the two processes has also been conducted and the parameters of the Arrhenius equation for the latter process have been estimated.

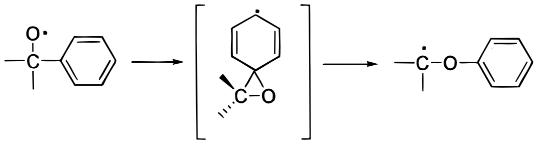
Introduction

The 1,2 migration of an aryl group in free radicals, known as the neophyl rearrangement,[2] has been extensively studied for 2-arylethyl radicals, and it is thought to occur via a spiro[2.5]octadienyl radical intermediate or transition state,[3] although direct detection for this type of intermediate has often failed. However, in at least one case[4] the intermediacy of a more stable spiro[cyclopropaneanthracen]-9-yl radical has been proved by ESR spectroscopy.

Similarly, the neophyl-like rearrangement of alkoxyl radicals, carrying at least two aryl substituents, is believed to proceed through a bridged-radical intermediate,[5,6] as shown in Scheme 1.

The direct detection, by time-resolved absorption spectroscopy, of the bridged intermediate for the 1,2 aryl migration of the 1,1-diphenylethoxyl radical was reported by Schuster,[5] but five years later Scaiano[6] demonstrated that the absorption band which Schuster attributed to the spiro[oxiranecyclohexadien]yl intermediate could instead be assigned to the starting alkoxyl radical.[7] Nevertheless, a series of AM1-UHF calculations which were also conducted[6] indicated that the bridged-radical is expected to be a "true" intermediate of this process and not only a transition state.

Scheme 1



We decided to study the mechanism of the neophyl-like rearrangement of the 1,1-diphenylethoxyl radical by ESR spectroscopy. Since the formation of the bridged intermediate could be thought to occur via the 1,3-*exo* cyclization of the alkoxyl moiety onto one double bond of the aromatic system, we chose to apply the same spin trapping technique which we had used for the detection of the oxiranylcarbinyl radicals formed by cyclization of the corresponding allyloxyl radicals.[8] But, when a solution of 1,1-diphenylethanol (**1**) and *t*-BuONO was photolyzed directly in the cavity of the ESR spectrometer, no signals were obtained, except for a weak one which was assigned to the adduct to *t*-BuONO of the cyanomethyl radical, deriving from H-abstraction of the *t*-BuO· from the solvent. The lack of detection of any radical species related to 1,1-diphenylethoxyl radical suggested that this method could not be exploited to achieve successfully the precursor alkoxyl radical, most likely due to the scarce efficiency of the exchange reaction between *t*-BuONO and aryl alcohols.[8,9]

Thus, a different procedure was considered in order to generate the alkoxyl radical.

Previous studies[10] conducted on the photoinduced oxidation of alcohols by CAN had demonstrated that,

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[1] In partial fulfillment of the requirements for a Ph.D. degree in Chemical Sciences, University of Bologna.

[2] Urry, W. H.; Kharasch, M. S. *J. Am. Chem. Soc.* **1944**, *66*, 1438.

[3] Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; pp 161−310.

[4] Leardini, R.; Nanni, D.; Pedulli, G. F.; Tundo, A.; Zanardi, G.; Foresti, E.; Palmieri, P. *J. Am. Chem. Soc.* **1989**, *111*, 7723.

[5] Falvey, D. E.; Khambatta, B. S.; Schuster, G. B. *J. Phys. Chem.* **1990**, *94*, 1056.

[6] Banks, J. T.; Scaiano, J. C. *J. Phys. Chem.* **1995**, *99*, 3527.

[7] (a) Avila, D. V.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 6576. (b) Avila, D. V.; Ingold, K. U.; Di Nardo, A. A.; Zerbetto, F.; Zgierski, M. Z.; Lusztyk, J. *J. Am. Chem. Soc.* **1995**, *117*, 2711.

[8] The allyloxyl radicals were obtained by photolysis of the corresponding nitrites, generated directly via an exchange reaction between the appropriate allylic alcohol and *tert*-butyl nitrite, which also acted as the spin trap: (a) Grossi, L.; Strazzari, S. *J. Chem. Soc., Chem. Commun.* **1997**, 917. (b) Grossi, L.; Strazzari, S.; Gilbert, B. C.; Whitwood, A. C. *J. Org. Chem.* **1998**, *63*, 8366.

[9] Doyle, M. P.; Terpstra, J. W.; Pickering, R. A.; LePoire, D. M. *J. Org. Chem.* **1983**, *48*, 3379.

10.1021/jo991856t CCC: $19.00

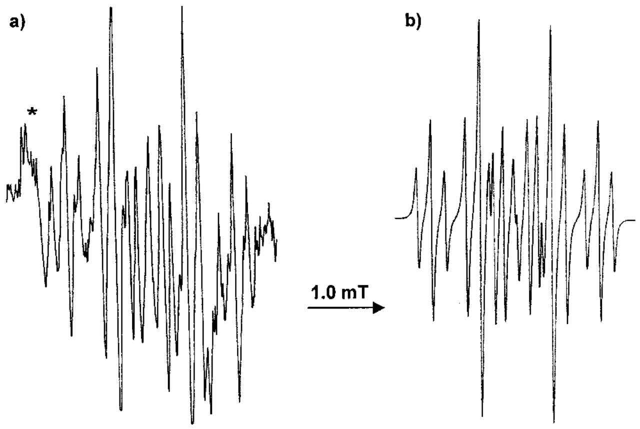


Figure 1. (a) ESR spectrum obtained in the photolysis of an acetonitrile solution of **1**, 20 mM, and CAN, 0.5 wt %, at 230 K, showing both radicals **2** and **3***. Spectrometer setting: microwave power, 7 mW; modulation amplitude, 0.1 mT; time constant, 2 s; gain, 2.5 × 10^4; scan range, 10 mT; scan time, 30 min. (b) Simulation of the spectrum of radical **2**.

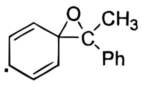
during this reaction, the corresponding alkoxyl radicals are formed. As a result, we considered it convenient to produce the alkoxyl radical of interest by photolysis of an acetonitrile solution of **1** and CAN directly in the ESR cavity.

Using the same procedure, experiments were also conducted on other aryl and naphthylcarbinols. The present study sets out the results obtained in the interaction of the analyzed substrates with this single electron oxidant.

Results and Discussion

(a) Photooxidation of 1,1-Diphenylethanol (1) with CAN. (i) Results. Acetonitrile solutions of **1**, 20 mM, and CAN, 0.5 wt %, were continuously flowed and irradiated (λ > 250 nm) directly in the cavity of an ESR spectrometer at low temperature (the best conditions were found at ca. 230 K). The procedure led to the detection of two different radical species (see Figure 1). The first radical, **2**, was characterized by hyperfine splitting constants conforming to those reported in the literature[11] for cyclohexadienyl-type radicals (Table 1); the second, **3**, showed an ESR pattern typical of a peroxyl radical (a sole broad line with a relatively high g-value, see Table 1). The mechanism of formation of these two species will be described later (vide infra).

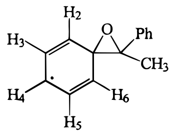
These findings led to assign to radical **2** a structure like that of a spiro[oxiranecyclohexadien]yl radical:



2

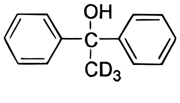
To obtain further evidence for the assignment of **2**, we performed two different experiments on two labeled compounds: the 1,1-diphenyl[2, 2, 2-$^2H_3$]ethanol (**4**) and the 1,1-[2′, 3′, 4′, 5′, 6′, 2″, 3″, 4″, 5″, 6″-$^2H_{10}$]diphenylethanol (**5**).

Table 1. ESR Hyperfine Splitting Constants (a/mT) of the Detected Radicals[a]

Radical	a	g[b]
 **2**	$a(H_4) = 1.005$ $a(H_3) = a(H_5) = 0.195$ $a(H_2) = a(H_6) = 0.675$	2.0053
3	-	2.0150
6	$a(D_4) = 0.156$ $a(D_3) = a(D_5) = 0.031$ $a(D_2) = a(D_6) = 0.108$	2.0053
7	-	2.0150
10	$a(H_4) = 1.008$ $a(H_3) = a(H_5) = 0.190$ $a(H_2) = a(H_6) = 0.671$	2.0053
11	-	2.0150
13	a (2H) = 2.173 a (3H) = 2.658	2.0026
15[c]	a (3H) = 2.250	2.0026
16[c]	a (2H) = 2.080 a (N) = 0.354	2.0029

[a] Typically at 230K. [b] ± 0.0002; the *g* factors have been determined by comparison with the *g* factor of the DPPH (2.0037 ± 0.0001). [c] At 283 K.

The photolysis of an acetonitrile solution of **4**, 20 mM, and CAN, 0.5 wt %, led to the same ESR spectrum (Figure 1) obtained in the photooxidation of **1**, thus indicating that there is no involvement of the methyl substituent in the structure of **2**. On the other hand, when **5** was analyzed in the same experimental conditions, it enabled the detection (see Figure 2a) of the peroxyl radical (**7**) (Table 1), as well as a second species assigned the structure **6** (Figure 2b). The latter was characterized by deuterium splittings each of ca. 1/6.5 that of the corresponding protons (Table 1).



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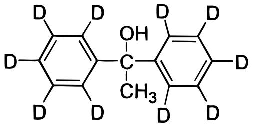
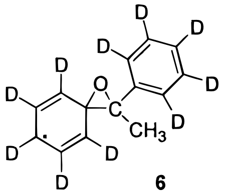
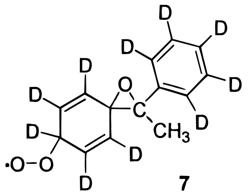


5



6



7

These experiments strongly supported the structure assigned to **2**, i.e., the same as the bridged intermediate

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(10) Grossi, L. *Res. Chem. Intermed.* **1996**, *22*, 315.
(11) Eiben, K.; Schuler, R. H. *J. Chem. Phys.* **1975**, *62*, 3093.

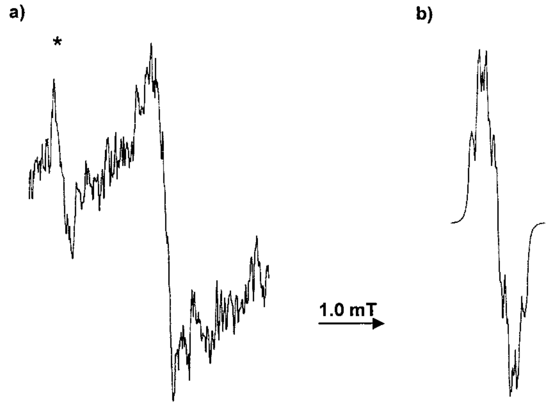


Figure 2. (a) ESR spectrum obtained in the photolysis of an acetonitrile solution of **5**, 20 mM, and CAN, 0.5 wt %, at 230 K, showing both radicals **6** and **7***. Spectrometer setting: microwave power, 7 mW; modulation amplitude, 0.1 mT; time constant, 2 s; gain, 2.5 × 10^4; scan range, 10 mT; scan time, 30 min. (b) Simulation of the spectrum of radical **6**.

in the neophyl-like rearrangement of the 1,1-diphenylethoxyl radical. However, since many unsuccessful attempts had been made to detect this intermediate by ESR,[12] further support for these spectroscopic results was required.

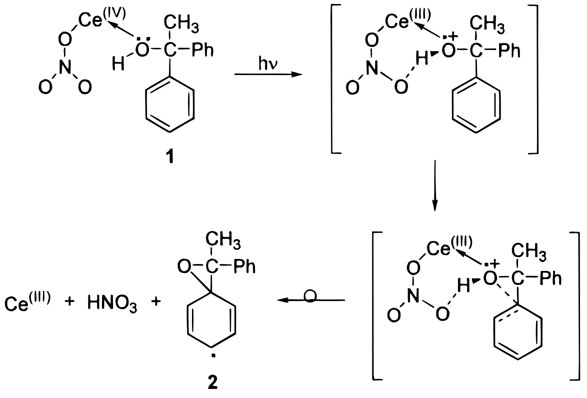
The 1,1-diphenylethoxyl radical was hence generated through an independent route, i.e., by photolysis of the corresponding 1,1-diphenylethyl peroxide (**8**).

An acetonitrile solution of **8**, ca. 25 mM, was flowed (flow rate: 3.5 mL/min) and directly photolyzed in the ESR cavity at 230 K: in these conditions, only the peroxyl radical **3** was detected.

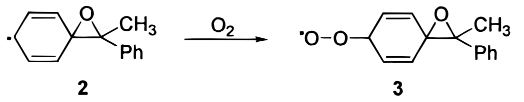
(ii) Mechanistic Interpretation. ESR detection of the 2-methyl-2-phenyl-1-oxaspiro[2.5]octa-4,7-dienyl radical (**2**) has never been reported before. We believe that, in the present study, an important role is played by CAN in the formation and in the stabilization of this intermediate. In fact, it is known[10] that in solution this nitrate salt can coordinate a tertiary alcohol molecule, leading to a 1:1 complex.[13,14] The electron-transfer process can thus be hyphotesized[10] to occur directly between the lanthanide in the excited state and the alcohol. The coordination of the oxygen of the hydroxyl group to the transition metal is expected to increase the electrophilicity of this moiety and, as a result, to favor the cyclization process (Scheme 2).

Most likely, the resulting bridged intermediate is stabilized inside the coordination sphere by additional interactions, for instance, by H-bonding between the hydrogen atom of the hydroxyl function and one oxygen atom of a nitrate ligand (see Scheme 2). In the absence of CAN, this extra stabilization is not present and the neophyl-like rearrangement proceeds so fast that it is not possible to detect radical intermediate **2**, for which a lifetime of less than 100 ns has been estimated.[6] This could account for the nondetection of **2** in the ESR experiments with the diphenylethyl peroxide (**8**).

Scheme 2



With regard to the mechanism of formation of the second detected species, **3**, since cyclohexadienyl radicals are known[7b,15] to react rapidly with oxygen to form the corresponding peroxyl radicals, it can be assumed that the traces of oxygen dissolved in the solution could quench the spiro[oxiranecyclohexadien]yl radical **2** to yield **3**, as shown below:



In the experiment on the diphenylethyl peroxide (**8**), however, two different peroxyl radicals could in principle be formed. The peroxyl species could in fact arise from quenching by oxygen of either the bridged intermediate **2** or the final product of the neophyl-like rearrangement, the 1-phenoxy-1-phenylethyl radical (see Scheme 1), which is also expected[15a] to react rapidly with oxygen. If the latter would be the case, it could explain the nondetection, by ESR, of this benzyl radical in such experiment.

It is noteworthy that the photooxidation of **1** by CAN did not lead to the detection of any radical species deriving from competitive β-scission processes. It is established that the 1,1-diphenylethoxyl radical does not undergo fragmentation,[5,7b] as a result of a faster carbon-to-oxygen migration of a phenyl group; similarly the CAN-induced cyclization seems to occur faster than the competitive β-scission processes.

(b) Photooxidation of Triphenylmethanol (9) with CAN. ESR experiments on acetonitrile solutions of **9**, 20 mM, and CAN, 0.5 wt %, at 230 K led to analogous results with those found for the 1,1-diphenylethanol (**1**), i.e., the detection of the 2,2-diphenyl-1-oxaspiro[2.5]octa-4,7-dienyl radical (**10**) and the corresponding peroxyl radical **11**, Table 1.

It is known[5] that the neophyl-like rearrangement for the triphenylmethoxyl radical is extremely fast compared to other reactions of alkoxyl radicals, thus, also in this case, a direct involvement of CAN in the mechanism of formation and stabilization of the bridged intermediate has to be invoked (Scheme 2).

(c) Photooxidation of 1,1-Diphenylpropanol (12) with CAN. The photolysis of a solution of **12**, 20 mM, and CAN, 0.5 wt %, in the same experimental conditions

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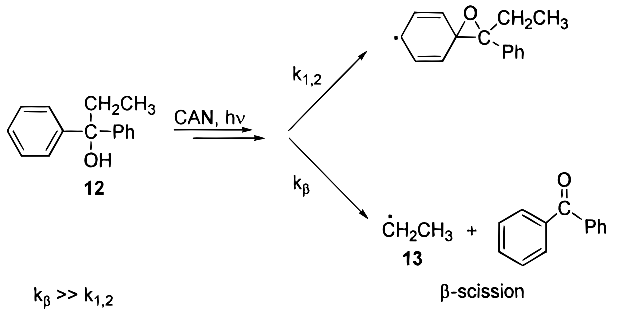
[12] (a) Kochi, J. K.; Krusic, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 3940. (b) Hamilton, E. J., Jr.; Fischer, H. *Helv. Chim. Acta* **1973**, *56*, 795. (c) Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 1224.

[13] Greatorex, D.; Kemp, T. J. *Trans. Faraday Soc.* **1971**, 56.

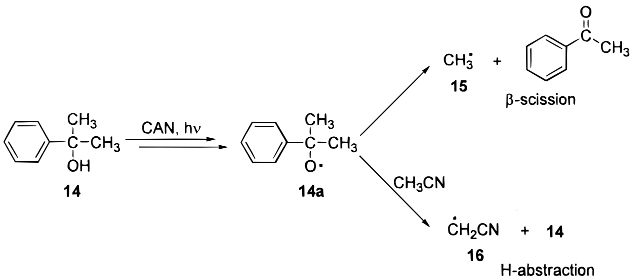
[14] The use of cerium(IV) as a qualitative colorimetric reagent for the detection of alcohols has been known for a long time and even quantitative methods for the analysis of alcohols based on the red color of the Ce(IV)–alcohol complexes have been developed: (a) Young, L. B.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1969**, *91*, 5060. (b) Trahanovsky, W. S.; Macaulay, D. B. *J. Org. Chem.* **1973**, *38*, 1497.

[15] (a) Maillard, B.; Ingold, K. U.; Scaiano, J. C.*J. Am. Chem. Soc.* **1983**, *105*, 5095. (b) Pan, X.-M.; Schuchmann, M. N.; von Sonntag, C. *J. Chem. Soc., Perkin Trans. 2* **1993**, 289.

Scheme 3



Scheme 4



used to analyze **1** and **9**, was performed directly in the ESR cavity. Only one radical species was detected: the ethyl radical (**13**), Table 1, deriving from a competitive β-scission process (Scheme 3).

No evidence for the formation of a spiro[oxiranecyclohexadien]yl radical could be obtained. This finding shows that, for the 1,1-diphenylpropyloxyl radical, even in the presence of CAN, the main process is the β-scission, which is evidently faster than the CAN-induced cyclization.

In the presence of traces of molecular oxygen in solution, we should expect the ethyl radical to react rapidly with O_2 to yield the corresponding peroxyl radical. But, in fact, we did not detect any peroxyl species, as it could be predicted, since it is known[10,16] that such type of radicals cannot be detected when the precursor alkyl radicals have low molecular weights, i.e., they have a short carbon atom chain ($n < 4$).

(d) Photooxidation of 2-Phenylpropan-2-ol, Cumyl Alcohol, (14) with CAN. (i) Results. When an acetonitrile solution of **14**, 50 mM, and CAN, 0.5 wt %, was continuously flowed (optimum conditions were found at 3.5 mL/min) and photolyzed inside the ESR cavity, two different radical species were detected (see Figure 3). Both species were generated in the competitive decay processes,[17,18] which the cumyloxyl radical can undergo (Scheme 4): the β-scission, yielding to the methyl radical (**15**), and the hydrogen abstraction from the solvent, which in this case leads to the cyanomethyl radical (**16**), Table 1.

The lack of detection of the bridged intermediate in this experiment indicated that its formation, in this case, is disfavored, even if mediated by CAN. This is consistent with the fact that the cumyloxyl radical is not expected to undergo the neophyl-like rearrangement,[5] as the radical species, which would arise from phenyl migration, could not be stabilized by conjugation with phenyl groups.

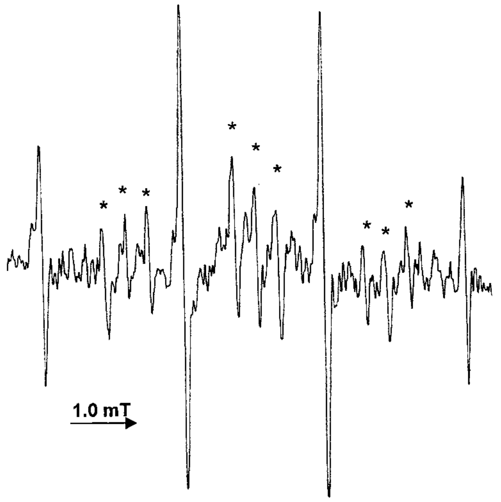


Figure 3. ESR spectrum obtained in the photolysis of an acetonitrile solution of **14**, 50 mM, and CAN, 0.5 wt %, at 283 K, showing both radicals **15** and **16***. Spectrometer setting: microwave power, 7 mW; modulation amplitude, 0.1 mT; time constant, 1 s; gain, 6.3 × 10^3; scan range, 10 mT; scan time, 16 min.

Table 2. Variation of the Ratio of Radicals [15]/[16] in Experiments on Acetonitrile Solutions of 14, 50 MM, and CAN, 0.5 wt %, as a Function of Temperature[a]

T (K)	[**15**]/[**16**]
268	76/24
273	73/27
276	70/30
283	69/31
291	65/35
293	60/40

[a] At fixed flow rate (3.5 mL/min).

Kinetic Studies. The ESR spectra obtained by photooxidation of **14** with CAN were recorded at variable temperature and, correspondingly, a variation of the relative concentrations of the two detected radical species as a function of the temperature was observed (Table 2). In particular, raising the temperature led to an increase in the proportion of H-abstraction (see Table 2), suggesting that this process is characterized by higher activation energy. This enabled us to conduct a study on the kinetic competition between the β-scission reaction and the H-abstraction from acetonitrile for the cumyloxyl radical.

Scheme 5 sets out[19] the reactions, which can be assumed to be involved in the whole process.

In the steady-state approximation:[20]

$$d[\mathbf{15}]/dt = k_2[\mathbf{14a}] - 2k_4[\mathbf{15}]^2 - 2k_5[\mathbf{15}]\,[\mathbf{16}] = 0 \quad (1)$$

$$d[\mathbf{16}]/dt = k_3'[\mathbf{14a}] - 2k_6[\mathbf{16}]^2 - 2k_5[\mathbf{15}]\,[\mathbf{16}] = 0 \quad (2)$$

Since it is established[21,22] that the bimolecular self-reactions of all simple alkyl radicals proceed at the

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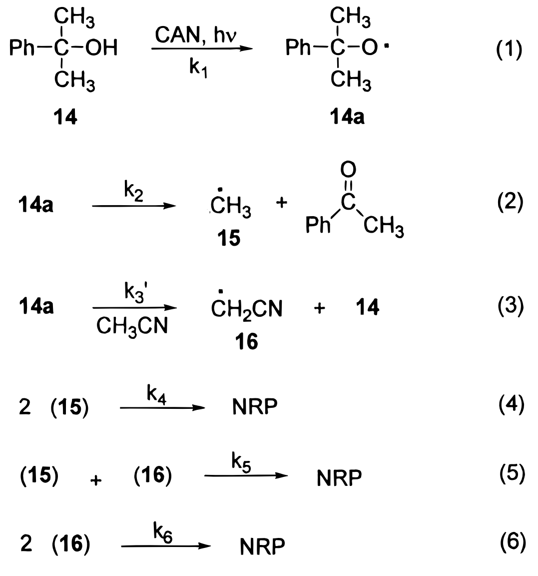
(16) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

(17) Walling, C. *Pure Appl. Chem.* **1967**, *15*, 69.

(18) (a) Baignée, A.; Howard, J. A.; Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 6120. (b) Avila, D. V.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466.

(19) In this scheme, radical–radical termination of two alkoxyl radicals and of an alkoxyl and a carbon centered radical, yielding respectively a peroxide and an ether, have not be included. These reaction can in fact be assumed to be relatively unimportant both for the very low steady-state concentration of the alkoxyl radical, which rapidly undergoes β-scission and H-abstraction, and for the low energies involved in the formed bonds. Also, reaction 2 can be considered to follow a pseudo-first-order kinetic equation, since acetonitrile, present as the solvent in large excess, can be assumed not to change its concentration significantly.

Scheme 5



NRP = Non Radical Products

Table 3. Variation of the Rate Constants of the Competitive Processes of β-scission (k_2) and H-Abstraction from CH_3CN (k_3') for the Cumyloxy Radical as a Function of Temperature

T (K)	$1/T$ (10^{-3} K^{-1})	k_2 (10^4 s^{-1})	k_3' (10^4 s^{-1})	log k_3'
293	3.41	36.3	24.2	5.38
291	3.44	32.4	17.5	5.24
283	3.53	20.3	9.12	4.96
276	3.62	13.2	5.65	4.75
273	3.66	10.9	4.02	4.60
268	3.73	7.83	2.47	4.39

diffusion-controlled limit (which means $k_4 = k_5 = k_6$), steady-state analysis leads to the simple relation:

$$k_3'/k_2 = [\mathbf{16}]/[\mathbf{15}] \qquad (3)$$

Hence, the ratio of the concentrations of the cyanomethyl radical (**16**) and the methyl radical (**15**) parallels the ratio of the kinetic constants of the H-abstraction and the β-scission processes.

The rate constant for the β-scission process of the cumyloxyl radicals, in acetonitrile, has been determined at 303 K [$k_2 = (6.3_3 \pm 0.4_3) \times 10^5$ s^{-1}][18b] and a value[18a] for the preexponential factor of log $A_2 = 12.4$ can be assumed for this reaction. Thus, it is possible to estimate the values of k_2 at different temperatures and, through eq 3, the corresponding values of k_3' (see Table 3).

A plot of log k_3' versus $1/T$ (see Table 3) should give a straight line with an intercept of logA_3' and a slope of $-(Ea_3'/2.303R)$, from which it should be possible to evaluate the parameters of the Arrhenius equation for the pseudo-first-order reaction of H-abstraction from acetonitrile for the cumyloxyl radical. When these data are plotted in this way, excellent agreement is observed (see Figure 4) and the following equation is obtained:

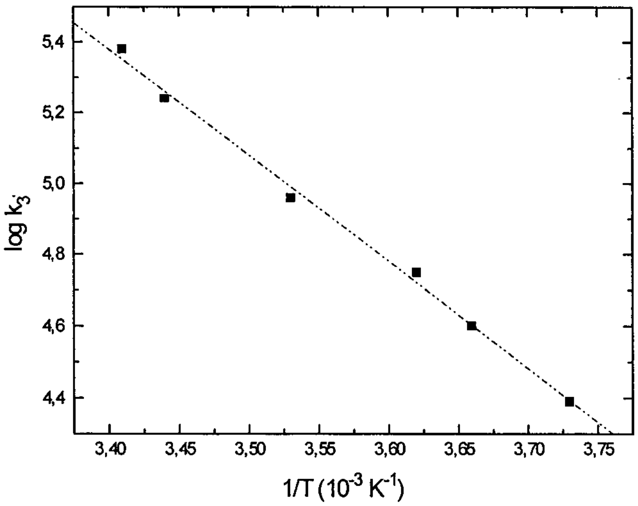


Figure 4. Log k_3' values vs $1/T$ (10^{-3} K^{-1}) in experiments on acetonitrile solutions of **14**, 50 mM, and CAN, 0.5wt %, at fixed flow rate (3.5 mL/min).

$$\log k_3' = (15.5_6 \pm 0.3_5) - [(13.7_2 \pm 0.4_5)]/\theta \qquad (4)$$

where $\theta = 2.303RT$ kcal/mol.

Thus, the activation energy for this process can be estimated as

$$Ea = (13.7_2 \pm 0.4_5)\ \text{kcal/mol}$$

and the value of k_3' at 303 K can be calculated from eq 4

$$k_3' = 4.81 \times 10^5\ \text{s}^{-1}$$

which sounds reasonable.

(e) Photooxidation of Naphthylcarbinols with CAN. The 1,2 migration of a 2-naphthylethyl radical is 2 orders of magnitude faster[21] than the analogous migration of an aryl group in 2-arylethyl radicals. For the former, in fact, the loss of stabilization for resonance, due to the formation of the bridged intermediate, is lower than that for the 2-arylethyl system. Thus, for a 2-naphthylethyl radical, the cyclization process, leading to a bridged-radical, is more favored, i.e., the activation energy for the formation of this intermediate is lower. Similarly, it is expected[23] that the neophyl-like rearrangement of an alkoxyl radical with a naphthyl substituent is even more favored than the analogous process for a phenyl-substituted alkoxyl radical.

Thus, experiments on the 2-(1-naphthyl)propan-2-ol (**17**) and the 1-naphthyldiphenylmethanol (**18**) were also performed. However, the photolysis of an acetonitrile solution of **17**, 30 mM, and CAN, 1 wt %, as well as that of a solution of **18**, 30 mM, and CAN, 1 wt %, did not allow the detection of any radical species.

Since no radical species were detected in these experiments, neither the bridged intermediates nor radicals deriving from competitive processes, such as β-scission or H-abstraction, we believe that only a weak interaction occurs between the α-naphthylcarbinols and CAN. Most likely, the coordination to the ceric ion of the hydroxyl

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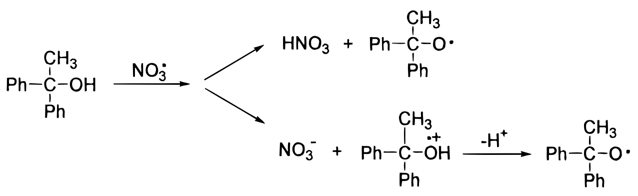
(20) The factor 2 in these equations has two different meanings (see ref 21). First, rate constants are generally defined in terms of the rate of formation of products, but in this system we are interested in the loss of reactants; actually, in reactions 4 and 6 two radicals **15** and two radicals **16**, respectively, are destroyed and so k_4 and k_6 must be multiplied by two. Second, the cross-termination reaction 5 is statistically favored by a factor of 2 (i.e., we have the same probability that radical **15** reacts with **16** as that **16** react with **15**) and hence k_5 must be multiplied by two.

(21) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(22) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 193.

(23) Neckers, D. C.; Linden, S.-M.; Taliano, R. J.; Williams, B. L.; Zakrzewski, D. *Tetrahedron Lett.* **1988**, *29*, 3029.

Scheme 6



function of these substrates cannot be accomplished due to steric hindrance. As a result, the formation of the complex, which seems to play an important role in the mechanism of production and stabilization of the bridged intermediate, cannot take place.

Conclusions

The ESR detection of the bridged-radicals **2** and **10**, which are believed[5,6] to be involved as intermediates in the neophyl-like rearrangements respectively of the 1,1-diphenylethoxyl and the triphenylmethoxyl radicals, has been obtained, by generating the precursor alkoxyl radicals by photooxidation of the corresponding alcohols, **1** and **9,** with CAN. Most likely, this nitrate salt favors the cyclization process, which leads to the bridged intermediates, by increasing the electrophilicity of the alkoxyl moiety by coordination. This accounts for the nondetection of such intermediates in the experiments with α-naphthyl derivatives, where the CAN-alcohol complex cannot be formed, probably due to steric hindrance.

In the absence of CAN, as in the experiment with 1,1-diphenylethyl peroxide (**8**), no evidence for the formation of **2** is obtained. This result leads to hypothesize that the bridged intermediate can be stabilized by interaction with CAN. If this stabilization lacks, the neophyl-like rearrangement proceeds fast and the bridged-radical cannot be detected due to its short lifetime.

A different mechanism for the formation of an alkoxyl radical from the interaction of the corresponding alcohol with CAN could also be taken into account. In fact, it is claimed[24] that, in the photolysis of CAN, a nitrate radical is produced:

$$\mathrm{Ce(IV)NO_3}^- \xrightarrow{h\nu} \mathrm{Ce(III)} + \mathrm{NO_3}^{\bullet}$$

This radical could then attack the hydroxyl function either by direct hydrogen abstraction or by electron transfer, leading in both cases to the corresponding alkoxyl radical (Scheme 6).

But, if that would be the case, we could not explained the fact that the naphthyl derivatives are not oxidized by CAN, since an intimate interaction should not be required. Moreover, this oxidation pathway does not lead to any extra-stabilization for the bridged intermediate; thus, we would not expect that the use of CAN could favor the formation of this radical, as it actually is.

The same procedure, i.e., the photooxidation by CAN, has been applied to the study of the 1,1-diphenylpropanol (**12**) and the cumyl alcohol (**14**). For these substrates, it has not been possible to detect the spiro[oxiranecyclohexadien]yl-type intermediates, probably because the rate of the cyclization process, mediated by CAN, is lower than the rates of competitive processes, which the corresponding alkoxyl radicals can undergo, such as β-scission and H-abstraction. Radical species deriving from the occurrence of these processes have been identified by ESR.

Finally, a kinetic study on the competition between the β-scission and H-abstraction decay processes for the cumyloxyl radical has been made. This study has led to estimate the parameters of the Arrhenius equation for the pseudo-first-order reaction of the H-abstraction from acetonitrile for the cumyloxyl radical [$\log A = (15.5_6 \pm 0.3_5)$; $\mathrm{Ea} = [(13.7_2 \pm 0.4_5)$ kcal/mol]].

Experimental Section

Materials. 1,1-Diphenylethanol, triphenylmethanol, 2-phenyl-2-propanol, and ceric ammonium nitrate (99.99% pure) were commercial products used as received. Acetonitrile was 99.9+% HPLC grade.

1,1-Diphenyl[2,2,2-^{2}H$_3$]ethanol (4). A suspension of turnings of Mg (22 mmol in 15 mL of anhydrous THF under an N_2 atmosphere) was gently refluxed in the presence of crystals of I_2 and ca. one-third of a solution of CD_3I (20 mmol in 5 mL of anhydrous THF) was added dropwise. The mixture was then warmed until the violet coloring, due to the iodine, disappeared. The remaining CD_3I was added and the solution refluxed for additional 30 min. Subsequently, the solution of the freshly prepared CD_3MgI was transferred in a three-necked flask by means of a long double-tipped deflecting needle so that the Grignard reagent could be easily separated from the excess of Mg. After dilution with 10 mL of anhydrous Et_2O, the mixture, kept under N_2, was cooled at −20 °C and then a solution of benzophenone (20 mmol in 10 mL of anhydrous Et_2O) was added dropwise. After stirring for 30 min at room temperature, the reaction was quenched with sat. NH_4Cl/H_2O and the organic layer extracted with Et_2O, dried over Na_2SO_4 and concentrated. The crude product was purified by chromatography on silica gel (petroleum ether/dichloromethane = 1:1): 2.44 g; 61%; mp 78−80 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 2.44 (1H, s, OH), 7.16−7.53 (10H, m); ^{13}C NMR (CDCl$_3$, 50.3 MHz) δ 30.5 (m, CD$_3$), 76.8 (C), 126.1 (CH), 127.5 (CH), 128.8 (CH), 148.1 (C); HRMS calcd for $C_{14}H_{11}D_3O$ 201.1233, found 201.1234.

1,1-[2′,3′,4′,5′,6′,2″,3″,4″,5″,6″-^{2}H$_{10}$]Diphenylethanol (5). To a stirred solution of bromobenzene-d_5 (11 mmol in 40 mL of anhydrous THF), kept at −50 °C and under an N_2 atmosphere, first *n*-butyllithium (12 mmol, 1.6 M in hexane) and then [2′, 3′, 4′, 5′, 6′-^{2}H$_5$]acetophenone (11 mmol in ca. 5 mL of anhydrous THF) were added dropwise. The mixture was allowed to react at room temperature (30−40 min), and subsequently the reaction was quenched with a saturated aqueous solution of NH_4Cl. After being extracted with Et_2O, the organic layer was dried over Na_2SO_4 and concentrated in vacuo. The purified product was obtained by chromatography on silica gel with CH_2Cl_2 as the eluent: 1.16 g; 52.1%; mp 73−76 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.91 (3H, s), 2.30 (1H, s, OH); ^{13}C NMR (CDCl$_3$, 50.3 MHz) δ 30.7 (CH$_3$), 76.1 (C), 125.4 (t, CD), 126.3 (t, CD), 127.6 (t, CD), 147.8 (C); HRMS calcd for $C_{14}H_4D_{10}O$ 208.1672, found 208.1674.

[2′,3′,4′,5′,6′-^{2}H$_5$]Acetophenone. 1-[2′, 3′, 4′, 5′, 6′-^{2}H$_5$]-Phenylethanol (17 mmol in 40 mL of CH_2Cl_2) was oxidized to the corresponding ketone with pyridinium chlorochromate 98% (3.75 g). The oxidation course was followed by thin-layer chromatography, and after 1 h, the reaction was quenched with Et_2O anhydrous. The organic phase was washed with Et_2O and separated from chromium salts by filtration. The solvent was removed under reduced pressure and the pure product recovered by chromatography on silica gel (petroleum ether/diethyl ether = 2:1): 1.34 g; 61.8%; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 2.58 (3H, s); ^{13}C NMR (CDCl$_3$, 50.3 MHz) δ 27.3 (CH$_3$), 128.9 (t, CD), 129.1 (t, CD), 133.7 (t, CD), 137.7 (C), 198.8 (C); HRMS calcd for $C_8H_3D_5O$ 125.0889, found 125.0890.

1-[2′,3′,4′,5′,6′-^{2}H$_5$]Phenylethanol. To a cooled solution (−50 °C) of phenyllithium-d_5 (30 mmol in 50 mL of anhydrous

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(24) (a) Baciocchi, E.; Del Giacco, T.; Rol, C.; Sebastiani, G. V. *Tetrahedron Lett.* **1985**, *26*, 541. (b) *ibidem*, 3353. (c) Del Giacco, T.; Baciocchi, E.; Steenken, S. *J. Phys. Chem.* **1993**, *97*, 5451.

THF under N_2), obtained by halogen−metal exchange from bromobenzene-d_5 (30 mmol) and *n*-butyllithium (32 mmol, 1.6 M in hexane), was added dropwise 3.4 mL of acetaldehyde (60 mmol in 5 mL of anhydrous THF). After additional stirring for 30−40 min at room temperature, the reaction was quenched with saturated NH_4Cl/H_2O and the mixture extracted with Et_2O. The organic layer was then dried over Na_2SO_4 and concentrated in vacuo. After chromatography on silica gel (petroleum ether/diethyl ether = 1:1) the desired product was obtained: 3.10 g; 81.4%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.43 (3H,d), 3.11 (1H, s, OH), 4.80 (1H, q); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 24.9 (CH_3), 69.9 (CH), 124.8 (t, CD), 126.6 (t, CD), 127.7 (t, CD), 145.6 (C); HRMS calcd for $C_8H_5D_5O$ 127.1045, found 127.1043.

1,1-Diphenylethyl Peroxide (8).[25] To a mechanically stirred solution of 1,1-diphenylethanol (20 mmol) dissolved in 60 mL of glacial acetic acid and 20 mL of Et_2O, kept under N_2 at 0 °C, was added dropwise hydrogen peroxide 30 wt % (10 mL), together with four drops of concentrated sulfuric acid. The reaction course was followed by thin-layer chromatography, and after ca. 8 h, the mixture was worked up by addition of an aqueous solution of NaOH, taking care that the temperature would not exceed 2/3 °C. The solution was then kept at −4 °C for 12 h, after which time the organic phase was extracted with Et_2O, washed with saturated $NaHCO_3/H_2O$, and dried over Na_2SO_4. The solvent was evaporated carefully under reduced pressure and the crude, consisting of a mixture of 1,1-diphenylethyl hydroperoxide and 1,1-diphenylethanol (70:30), used without further purification. In the second step of the synthesis, the mixture of hydroperoxide and alcohol was suspended in 100 mL of formic acid 90% and stirred for ca. 4 h. The formation of the peroxide was checked by thin-layer chromatography. The solution was kept at −4 °C overnight so that the peroxide could slowly precipitate. The solid phase was then filtered, washed with distilled water and dissolved in Et_2O. The obtained solution was dried over Na_2SO_4 and concentrated in vacuo. The residue was crystallized twice from petroleum ether and benzene, yielding the pure product: 1.65 g; 41.9%; mp 148−150 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.98 (6H, s), 7.25 (20H, s); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 27.0 (CH_3), 86.7 (C), 127.7 (CH), 127.8 (CH), 128.4 (CH), 145.7 (C).

1,1-Diphenylpropanol (12). To a solution of benzophenone (14 mmol in 30 mL of anhydrous THF), stirred under N_2 and cooled at −50 °C, was added dropwise ethylmagnesium bromide (5 mL, 15 mmol, 1.0 M in THF). The reaction mixture was allowed to warm to room temperature and, after 50 min, was quenched with saturated NH_4Cl/H_2O. The organic phase was then extracted with Et_2O and dried over Na_2SO_4. The solvent was removed under reduced pressure and the product isolated by chromatography on silica gel (petroleum ether/diethyl ether = 3:1): 2.10 g; 67.7%; mp 95−96 °C (lit.[26] mp 95 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.87 (3H, t), 2.08 (1H, s, OH), 2.31 (2H, q), 7.15−7.46 (10H, m); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 8.7 (CH_3), 34.9 (CH_2), 79.0 (C), 126.6 (CH), 127.3 (CH), 128.6 (CH), 147.4(C).[27]

1-Naphthyldialkylmethanols. The 2-(1-naphthyl)propan-2-ol (**17**) was prepared according to a literature method.[28] The 1-naphthyldiphenylmethanol (**18**) was synthesized adopting the same procedure:[28] 2.99 g; 69%; mp 135−136 °C (lit.[29] mp 134−135 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.32 (1H, s, OH), 6.85 (1H, d), 7.20−7.42 (13 H, m), 7.82 (2H, t), 8.08 (1H, d); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 84.0 (C), 124.9 (CH), 126.0 (CH), 126.2 (CH), 127.8 (CH), 128.4 (CH), 128.7 (CH), 128.9 (CH), 129.5 (CH), 130.0 (CH), 131.9 (C), 135.6 (C), 142.7 (C), 147.6 (C); HRMS calcd for $C_{23}H_{18}O$ 310.1358, found 310.1362.

ESR Experiments. The acetonitrile solutions of the arylcarbinols (10−50 mM) and CAN (0.5−1wt %) were purged with gaseous N_2 for at least 45 min before use. The mixtures were then continuously flowed (flow rate 2.0−3.5 mL/min) through a flat quartz cell (0.3 mm width) inside an ESR cavity and directly irradiated with an OSRAM HBO 500 W/2 high-pressure mercury lamp. A Varian E−104 spectrometer, equipped with a variable temperature control system, was used. The temperatures inside the spectrometer cavity, in the kinetic experiments, were calibrated by means of a Ni/Cu thermocouple inserted into the flat quartz cell after the spectral measurements. Relative radical concentrations and hyperfine splitting assignments were obtained by means of computer simulations.

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[25] The synthesis of this substrate was performed following a procedure suggested by Prof. R. Leardini.

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