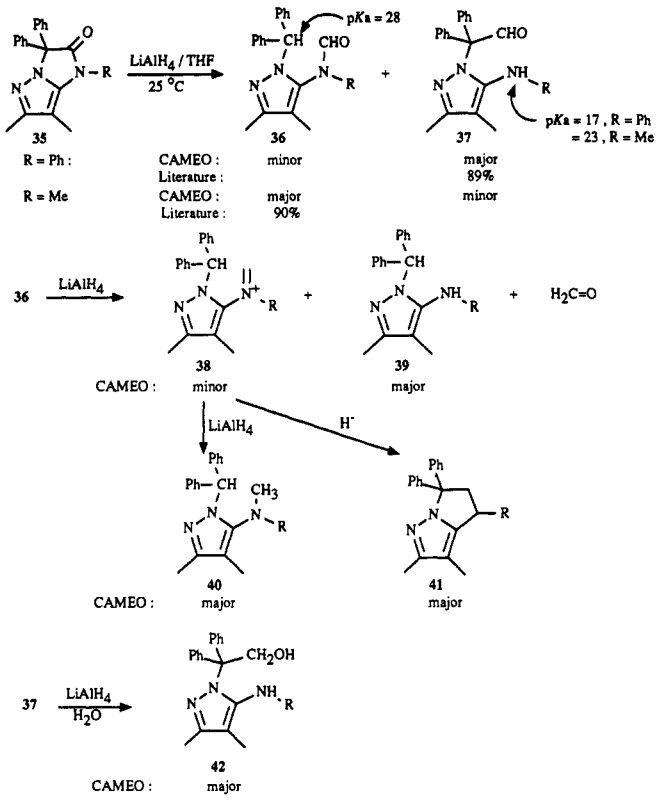
**Scheme VI**




anions is greater than 8, then C–N cleavage is favored; otherwise, C–C cleavage becomes the predominant pathway. Thus, when R is changed from an aryl to an alkyl group, C–C cleavage becomes more favored, and compound **36** is displayed with a major product designation. Resubmission of **36** under 1-equiv conditions yields the iminium ion intermediate **38** and the secondary amine **39** in minor and major amounts, respectively. It must be recalled that with nucleophilic hydrides, iminium ion formation is normally not favored unless an elevated reaction temperature is specified (see section III.E.3). Resubmission of **38** under 1-equiv conditions gives the tertiary amine **40**. The reported products in the literature for the reduction of **36** include the cyclic amine **41** in addition to amines **39** and **40**. The redox module does not output the former product since it arises from a nonreductive process. However, this product may be obtained upon submission of intermediate **38** to the nucleophilic module with hydride anion as the input reagent. Finally, resubmission of **37** to the redox module gives the amino alcohol **42**. Note that with first selectivity conditions, reduction of **35** leads directly to **36** and **42**, and reduction of **36** leads directly to **39** and **40**.

## V. Conclusion

The reductive chemistry of a representative variety of synthetically useful hydride reagents has been implemented in the CAMEO program. This required a systematic analysis of numerous reactions in terms of basic mechanistic steps. The recognition of these steps, which are shared by both nucleophilic and electrophilic hydrides, is crucial to the development of efficient algorithms for evaluating reductions. Mechanistic analyses are applied to determine (a) the reactivity of a given site, (b) the chemoselectivity of the hydride reagent, (c) the regiochemistry of hydride attack on specific sites, and (d) the preferred routes in multipathway transformations. Existing algorithms in CAMEO for calculating parameters such as frontier molecular orbital energies, bond dissociation energies, ion stabilities, $pK_a$'s, and Taft $E_s$ parameters are utilized during reaction evaluation. Additionally, reactivity tables with general utility were developed for the covered reagents to address competitions among potentially reactive sites. Finally, a modular approach in the implementation of hydride reductions has been undertaken to accommodate transformations with currently unknown mechanisms.

**Acknowledgment.** Gratitude is expressed to the National Science Foundation for support of this work. Thanks are also due to Daniel L. Severance for his assistance in the development of algorithms.

# Electron-Transfer Reactions. Oxidation of Grignard Reagents in the Presence of an Aminoxyl as a Radical-Trapping Agent

Patricia Carloni, Lucedio Greci,* and Pierluigi Stipa

*Dipartimento di Scienze dei Materiali e della Terra, Università di Ancona, Via Brecce Bianche, I-60131 Ancona, Italy*

Lennart Eberson*

*Organic Chemistry 3, Chemical Center, University of Lund, P.O. Box 124, S-22100 Lund, Sweden*

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The indole bisnitrone **1** ($E_{1/2}$red = −0.125 V vs NHE in DMF) reacts with a series of Grignard reagents (RMgX) including primary, secondary, and tertiary alkyls and benzyl and phenyl derivatives, which show different $E_{ox}$, by single electron transfer to form C-centered radicals corresponding to the Grignard used. The radicals produced in the reaction were trapped by the (arylimino)indolinone nitroxide **5** to form the alkylated hydroxylamines **6**. When the reaction is carried out with a "cyclizing Grignard" such as 5-hexenylmagnesium bromide, the uncyclized (5-hexen-1-yl) **6g** and cyclized (methylcyclopentyl) **6h** alkylated hydroxylamines are both isolated. In all cases, the Marcus theory treatment predicts high electron-transfer rate constants.

The reactions of Grignard reagents with organic substrates have been widely studied from the synthetic point of view,[1] and it can be safely asserted that their role in this respect has not yet been exhausted. During the last

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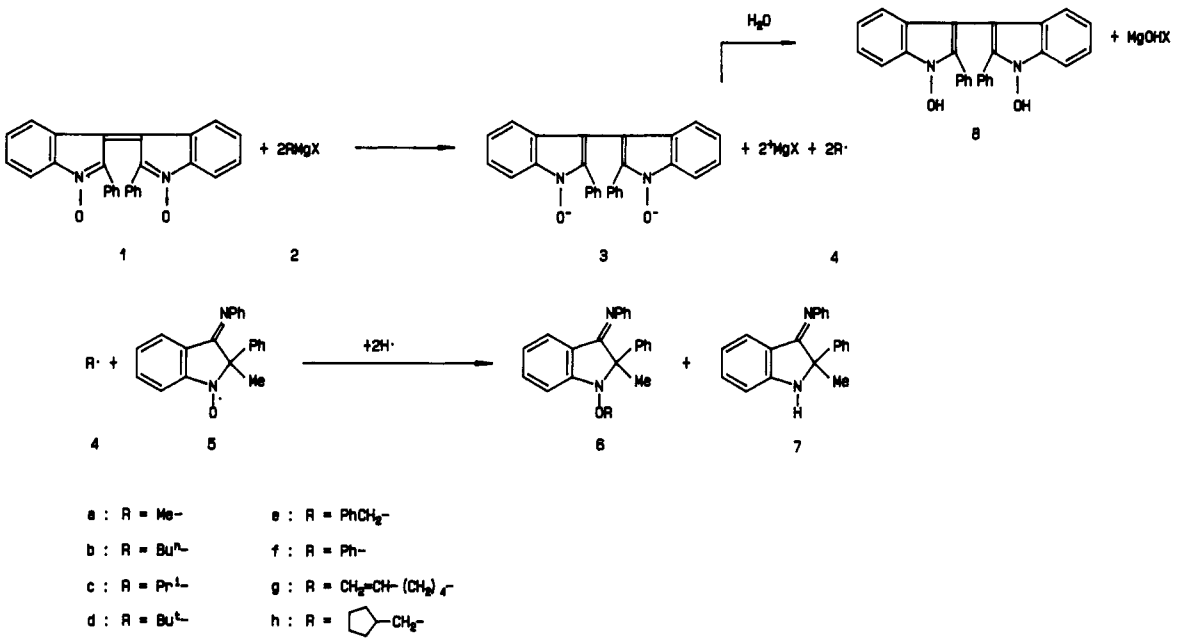
Scheme I



a : R = Me– e : R = $PhCH_2$–
b : R = $Bu^n$– f : R = Ph–
c : R = $Pr^i$– g : R = $CH_2$=CH–$(CH_2)_4$–
d : R = $Bu^t$– h : R = –$CH_2$–

two decades, these reactions also received great attention from the mechanistic point of view;[2] in particular, the nucleophilic addition and the electron transfer (ET) are still objects for discussion.

Some years ago, we observed that the reaction between a Grignard reagent and an indolenine system[3] involves ET, as judged from a consideration of product distributions. More recently, the reaction was repeated with 5-hexenylmagnesium bromide and shown to yield a cyclopentylmethyl-substituted product, thus demonstrating that the reaction does involve an ET mechanism in competition with the conventional one of nucleophilic attack.[4a] The latter results were supported by the application of the Marcus theory of outersphere ET.[4] Later, in an attempt to define better the borderline between ET and nucleophilic addition,[4b] we studied the reactions of a number of quinoline *N*-oxides, possessing redox potentials for one-electron reduction in a suitable potential range, with Grignard reagents. By comparison of the experimental results (ratio of noncyclized/cyclized products from 5-hexenylmagnesium bromide) with theoretical ones (again based on the Marcus theory), we established that a substrate (S) with a $S/S^{\bullet-}$ redox potential less negative than –0.8 V[5] was able to oxidize an alkylmagnesium halide with an $RMgX^{\bullet+}/RMgX$ redox potential of <–0.52 V. Of course, this conclusion must take into account the imperfection of the scale of redox potentials for Grignard reagents, influenced by both very fast chemical follow-up reactions and strongly irreversible electrochemical behavior.[4c,d]

This paper reports the results of a study of the reactions between the indole bisnitrone **1**, the $S/S^{\bullet-}$ redox potential of which is –0.16 V in DMF, and a series of Grignard reagents of different $RMgX^{\bullet+}/RMgX$ redox potentials. It is shown that **1** acts as a one-electron oxidant toward all RMgX employed in this study, including the most difficultly oxidizable one, PhMgX.

Table I. Yields of Isolated Product in the Reaction of 1 with 2 in the Presence of 5

| reactants | products (% yield) |
|---|---|
| 1 + 2a | 5 (28); 6a (59); 7 (7) |
| 1 + 2b | 5 (10); 6b (75); 7 (5) |
| 1 + 2c | 5 (22); 6c (49); 7 (21) |
| 1 + 2d | 5 (15); 6d (38); 7 |
| 1 + 2e | 5 (15); 6e (69); 7 (7) |
| 1 + 2f | 5; 6f (4); 7 (60) |
| 1 + 2g | 5 (28); 6g (24); 6h (13); 7 (16) |

## Results

The reactions between the indole bisnitrone **1** and Grignard reagents **2** in the presence of a radical trap, aminoxyl **5**, were carried out in tetrahydrofuran (THF) or THF/diethyl ether at room temperature, adding the Grignard solution dropwise to the mixture of **1** and **5** with the components **2**, **1**, and **5** in a 2:1:1 molar ratio (Scheme I). Since the reaction between **1** and **2** is instantaneous, the Grignard reagent, prepared in slight excess, was added until the color of the initially black bisnitrone solution has disappeared completely. By this procedure, we assume that the stoichiometric amount of Grignard reagent with respect to the bisnitrone (2:1 required) has been supplied. After hydrolysis of the reaction mixture, the content of the orange-colored organic layer was identified as a mixture of the dihydro derivative **8**, the alkylated hydroxylamine **6**, the 3-(arylimino)indolenine **7** and the starting aminoxyl **5**. Since compound **8** easily autoxidized to the starting material **1**, the whole reaction mixture was oxidized with lead dioxide before the final product analysis. It was separately established that none of the other components was affected by this procedure. The products (Table I) were then separated by column chromatography or preparative TLC.

(1) (a) Eicher, *The Chemistry of the Carbonyl Group*; Patai, S., Ed.; ref 40, pp 621–693. (b) Kharasch, M. S.; Rheinmuth, O. *Grignard Reactions of Nonmetallic Substances*; Prentice-Hall; Englewood Cliffs, NJ 1954; pp 138–528.

(2) (a) Walling, C. *J. Am. Chem. Soc.* **1988**, *110*, 6846 and references cited therein. (b) Okubo, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3108. (c) Holm, T. *Acta Chem. Scand.* **1983**, *B37*, 567. (d) Dogonneau, M. *Bull. Soc. Chim. Fr* **1982**, 269. (e) Ashby, E. C.; Bowers, J. R., Jr; *Aust. Chem. Soc.* **1981**, *103*, 2242. (f) Gough, R. G.; Dixon, J. A. *J. Org. Chem.* **1968**, *33*, 2148.

(3) (a) Berti, C.; Greci, L.; Marchetti, L. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1032; (b) *Ibid.* **1979**, 233.

(4) (a) Eberson, L.; Greci, L. *J. Org. Chem.* **1984**, *49*, 2135. (b) Eberson, L.; Cardellini, L.; Greci, L.; Poloni, M. *Gazz. Chim. Ital.* **1988**, *118*, 35. (c) Eberson, L. *Acta Chem. Scand.* **1984**, *B38*, 439. (d) Eberson, L. *Electron Transfer Reaction in Organic Chemistry*; Springer-Verlag: Heidelberg, 1987.

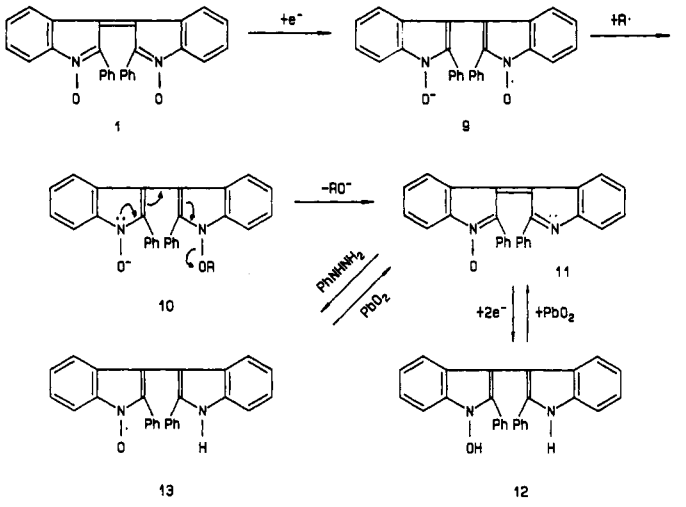
(5) All potentials are given vs the normal hydrogen electrode (nhe).

**Table II. Spectroscopic Data of Compounds 6a–h**

| compds | mp (°C) | formula | MW | IR $\nu_{max}$ ($cm^{-1}$) | δ (in $CDCl_3$) | mass m/e (rel int) |
|---|---|---|---|---|---|---|
| **6a** | | $C_{22}H_{20}N_2O$ | 328 | 1660, 1600, 755, 695[a] | 1.92 (s, 3 H); 3.7 (s, 3 H); 6.36–7.63 (m, 14 H, arom) | 328 ($M^+$, 8), 297 (100) |
| **6b** | | $C_{25}H_{26}N_2O$ | 370 | 1660, 1600, 755, 695[b] | 0.78 (t, 3 H, $J$ = 7 Hz); 1.28–1.63 (m, 4 H); 1.95 (s, 3 H); 3.80 (m, 2 H); 6.14–7.62 (m, 14 H, arom) | 370 ($M^+$, 5), 297 (100) |
| **6c** | | $C_{24}H_{24}N_2O$ | 356 | 1660, 1600, 755, 695[a] | 1.04 (d, 3 H, $J$ = 6 Hz); 1.26 (d, 3 H, $J$ = 6 Hz); 1.94 (s, 3 H); 3.8 (m, 1 H), 6.2–7.57 (m, 14 H) | 356 ($M^+$, 9), 297 (100) |
| **6d** | | $C_{25}H_{26}N_2O$ | 370 | 1660, 1600, 755, 695[a] | 1.08 (s, 3 H); 1.88 (s, 3 H); 6.36–7.43 (m, 14 H, arom) | 370 ($M^+$, 7), 297 (100) |
| **6e** | 56 | $C_{28}H_{24}N_2O$ | 404 | 1660, 1600, 755, 695[a] | 1.98 (s, 3 H); 4.72 (s, 2 H); 6.3–7.8 (m, 19 H, arom) | 404 ($M^+$, 10), 211 (100) |
| **6g + 6h** | | $C_{27}H_{28}N_2O$ | 396 | 1660, 1600, 755, 695[b] | 0.92–2.19 (m, 14 H); 1.94 (s, 3 H); 3.48–4.0 (m, 4 H); 4.89 (b s, 1 H); 5.02 (b d, 1 H); 5.52–6.02 (m, 1 H); 6.36–7.62 (m, 28 H, arom) | 396 ($M^+$, 5), 297 (100) |

[a] Nujol. [b] Neat.

**Scheme II**




Compounds **6**, which were very difficult to obtain in the crystalline state, were identified by their spectroscopic data (Table II). They all gave rise to a molecular ion peak in their mass spectra and a fragmentation pattern in agreement with the assigned structure. The IR spectra showed absorptions at 1600 and 1660 $cm^{-1}$, typical of the PhN(OR)C< [6] and >C=N— [3a] groups. The $^1H$ NMR spectra showed aromatic proton signals identical for all derivatives, whereas differences were attributable to the R group of the NOR function (Table II). Compound **7** was identified by comparison with an authentic sample.[3] In the case of the reaction with 5-hexenylmagnesium bromide (**2g**), the alkylated hydroxylamine was a mixture of two isomers, **6g** and **6h**, the ratio of which (**6g**:**6h** = 2) was determined by both HPLC analysis and $^1H$ NMR spectroscopy.

In some cases, compound **11** (the mononitrone corresponding to **1**) was isolated in trace amounts together with **1** regenerated by lead dioxide treatment of the reaction mixture. This compound was identified either by comparison with an authentic sample[7] or by the ESR signal of radical **13**, a characteristic product of **11** upon reduction by $^1/_3$ equiv of phenylhydrazine (Scheme II).[7] The structure was additionally confirmed by reoxidation of **13** to **11** by lead dioxide.

## Discussion

As stated in the introduction, the expected products from the reaction between **1** and Grignard reagents **2a–g** might have been those of nucleophilic attack of RMgX upon the *N*-oxide functions of **1** or those resulting from a redox process, initiated by an initial ET between **1** and **2**. Since it has been observed that the reaction involves ET, forming radical species, our aim was to find a suitable radical scavenger to trap the R• generated by one-electron transfer from RMgX and simultaneous/subsequent cleavage of the C–Mg bond. The best radical scavengers, namely 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO)[10] and *N*-*tert*-butyl-α-phenylnitrone (PBN),[10] could not be used because of their high reactivity toward Grignard reagents leading to persistent aminoxyls without providing evidence for possible radical pathways of the reaction under study.[11] Considering that aminoxyls rapidly react with alkyl radicals to yield alkylated hydroxylamines, the reactions were carried out in the presence of aminoxyl **5**, which reacts with neither RMgX nor the bisnitrone **1**.

The fact that compounds **6a–h** always were the main products from the reactions studied suggests that the ET mechanism is predominant in all cases. This means that in the most extreme case an organic substrate with an $S/S^{\bullet-}$ redox potential of −0.16 V can oxidize phenylmagnesium bromide, which is the most difficultly oxidizable RMgX or Table III. These results are easily rationalized on the basis of the Marcus theory[4d,11a] for estimating rate constants of outersphere electron transfer reactions, the application of which on reactions of Grignard reagents is described in detail in ref 4a.

(6) Witkop, B.; Patrick, J. B. *J. Am. Chem. Soc.* **1951**, *73*, 713.
(7) Bruni, P.; Poloni, M. *Gazz. Chim. Ital.* **1970**, *200*, 1119.
(8) Andruzzi, R.; Trazza, A.; Bruni, P. *Electroanal. Chem. Inter. Electrochem.* **1974**, *51*, 341.
(9) Lal, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6355.
(10) (a) Perkin, M. J. Spin Trapping In *Adv. Phys. Org. Chem.* **1980**, *17*, 1. (b) Zubarev, V. E.; Belevskii, V. N.; Bugaenko, L. T. *Russ. Chem. Rev.* **1979**, *48*, 1361.
(11) It is well-known that Grignard reagents add to nitrones or cyclic *N*-oxides to form the hydroxylamine precursors of aminoxyls: see ref 4b and references cited therein. (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (b) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

Table III. Calculations of log ($k_{ET}$, $M^{-1}$ $s^{-1}$) for Reactions between 1 and RMgX, Using the Marcus Approach[a]

| R in RMgX | $E°$ ($RMgX^{•+}$/RMgX)[b] (V) | $\Delta G°$ (kcal/mol) | λ (kcal/mol) 40 $\Delta G^{‡}$ (kcal/mol) | 40 log ($k_{ET}$) | 65 $\Delta G^{‡}$ (kcal/mol) | 65 log ($k_{ET}$) |
|---|---|---|---|---|---|---|
| Me | −0.25 | −11.1 | 5.2 | 7.2 | 11.2 | 2.8 |
| Bu | −0.53 | −17.5 | 3.2 | 8.7 | 8.7 | 4.6 |
| $Pr^{i}$ | −0.95 | −27.2 | 1.0 | 10.3 | 5.5 | 7.0 |
| $Bu^{t}$ | −1.07 | −30.0 | 0.6 | 10.6 | 4.7 | 7.6 |
| $PhCH_2$ | −0.73 | −22.1 | 2.0 | 9.5 | 7.1 | 5.8 |
| Ph | 0.0 | −5.3 | 7.5 | 5.5 | 13.7 | 1.0 |

[a] Equation 1, using an electrostatic correction term of −9.0 kcal/mol. [b] References 2c and 4d.

The results of Marcus-type calculations are shown in Table III. The standard free energy change of the putative ET step was corrected by an electrostatic term of −9.0 kcal $mol^{-1}$ (corresponding to a transition state with the centers of the reacting species at a distance of 5 Å, embedded in a medium of dielectric constant 7.4 (THF)). This gave the $\Delta G°'$ values of column 3 (Table III) then used to compute $\Delta G^{‡}$ by the Marcus expression (eq 1) with the reorganization energy λ(0) of the $RMgX^{•+}$/RMgX couple varying between the extremes of 70 and 120 kcal $mol^{-1}$. This range

$$\Delta G^{‡} = \lambda/4\,(1 + \Delta G°'/\lambda)^2 \qquad (1)$$

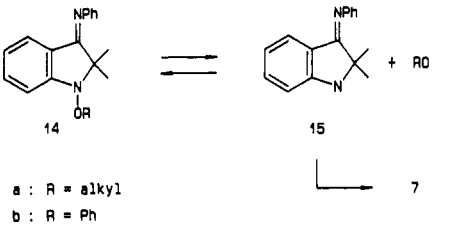
of λ(0) was previously found in preliminary attempts to fit rate data for ET reactions of Grignard reagents to the Marcus treatment.[4c,d] The reorganization energy of $1/1^{•-}$ was taken to be low, 10 kcal $mol^{-1}$, as commonly found for aromatic and heteroaromatic systems.[11b] Thus, the extremes of the reorganization energy λ of the ET step at hand were 40 and 65 kcal $mol^{-1}$. The corresponding $\Delta G^{‡}$ and log ($k_{ET}$) values were shown in Table III.

In all cases, even for the least favorable one of PhMgBr, the Marcus treatment predicts high or reasonably high ET rate constants for the 1/RMgBr reaction, entirely in agreement with our experimental results.

The feasibility of the ET between 1 and a Grignard reagent with an $RMgX^{•+}$/RMgX potential around −0.5 V was further verified by the use of a radical probe capable of cyclizing during the reaction, namely 5-hexenylmagnesium bromide. It is well-known that the 5-hexenyl radical cyclizes with a rate constant of $10^5$ $s^{-1}$;[8] so that the presence of **6h** among the reaction products is an additional diagnostic of ET. In this case, the formation of **6g** and **6h** in a 2:1 ratio is particularly significant. The radical trapped by the aminoxyl **5** is trapped outside the solvent cage in which it is formed. The results obtained fit well with the 5-hexenyl radical cyclization rate and the rate of coupling with **5**, known to be nearly diffusion controlled.[12] In line with these considerations, an increase of the proportion of the cyclized derivative **6h** was obtained in more dilute solutions; in fact, using a half concentration of the reactants the **6g**:**6h** ratio decreased to 1.6 from 1.9.

Table I shows that the main reaction product is **6**, together with minor amounts of amine **7**, for all cases involving RMgX with R = alkyl. For R = phenyl, amine **7** was the predominant product. We believe that **7** is formed from the corresponding alkylated hydroxylamine **6** but have difficulties in formulating a reasonable mechanism. In principle, **7** could also be formed from the nitroxide **5** by a disproportionation reaction; however, this is excluded by the fact that the quinone *N*-oxide that should be formed simultaneously has never been observed.[13] Instead, we

**Scheme III**




propose that the homolytic cleavage of the N–OR bond of **6** (Scheme III) is favored for R = Ph. The elimination of a phenoxy radical is thermodynamically more favored than that of an alkoxy radical. Thus, the arylated hydroxylamine **6f** is formed in low yield only.

A final comment on the indole bisnitrone **1** is in order. As we have already stated in the Results, **1** is reduced to dianion **3** by the Grignard reagent. Species **3** is then hydrolyzed to **8**, which is reoxidized to **1** by lead dioxide. In some cases, traces of compound **11** were also isolated; since this compound is black too, it can be argued that **11** is formed from **12** during reoxidation. Compound **11** was, however, transformed into the corresponding nitroxide **13** by reduction and **13** into **11** by lead dioxide oxidation. By these crossing experiments we have identified and explained the route to formation of **11**.

## Experimental Section

Melting points are uncorrected. ESR spectra were recorded on a Varian E4 spectrometer and $^1H$ NMR spectra on a Varian XL 100 using TMS as internal standard. IR spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer. Liquid chromatography was performed on a Perkin-Elmer Series 2 HPLC and gas chromatography on a Carlo Erba MEGA HRGC 5150 GC.

Compounds **1**[14] and **5**[15] were prepared as described in literature. The halides and the magnesium were Aldrich commercial products.

**Reaction of 1 with Grignard Reagents in the Presence of Aminoxyl 5. General Procedure.** The Grignard reagents were prepared by the usual method starting from the halides (5 mmol in 10 mL of THF or $Et_2O$) and magnesium (0.12 g, 5 mmol in 5 mL of THF or $Et_2O$).[16] The Grignard solution was added to the solution of **1** (0.207 g, 0.5 mmol) and **5** (0.157 g, 0.5 mmol) in 20 mL of THF at room temperature under stirring and under a nitrogen atmosphere until the disappearance of the dark color of the solution. After 1 h, the reaction mixture was poured into a 0.1 M solution of $NH_4Cl$ (50 mL) and extracted with $CH_2Cl_2$

(12) (a) Beckwith, A. L.; Bowwry, V. W.; Moad, G. *J. Org. Chem.* **1988**, *53*, 1632. (b) Chateauneuf, J.; Lusztjk, J.; Ingold, K. U. *J. Org. Chem.* **1988**, *53*, 1629.

(13) Greci, L. *Tetrahedron* **1982**, *39*, 677.

(14) Colonna, M.; Greci, L. *Gazz. Chim. Ital.* **1969**, *99*, 351.

(15) Berti, C.; Colonna, M.; Greci, L.; Marchetti, L. *Tetrahedron* **1975**, *31*, 1745.

(16) The 5-hexenylmagnesium bromide prepared following our method contained 3–4% of (cyclopentylmethyl)magnesium bromide: the percentage was determined by GC through the ratio of the 1-hexene and methylcyclopentane obtained by hydrolysis of the Grignard reagents mixture. GC conditions: column, Phase SPB-5 0.25 μm, 30 m × 0.25 mm; injection, 2 μL, split ratio 1/100; detector, FID 330 °C; injector, 280 °C; conditions, isothermal 30 °C, flow: $N_2$ 10 cm/s.

(2 × 50 mL). The organic layer was dried over $Na_2SO_4$ and oxidized with $PbO_2$ (0.5 g) under stirring. After 0.5 h, the insoluble salts were filtered off, the filtrate was evaporated to dryness, and the residue was chromatographed on a $SiO_2$ column, eluting with light petroleum/ethyl acetate (95:5).

**HPLC Measurements. General Procedure.** The Grignard reagents were prepared starting from the halides (0.5 mmol in 5 mL of THF or $Et_2O$) and magnesium (0.12 g, 0.5 mmol in 5 mL of THF or $Et_2O$) and adding to the solution of 1 (0.052 g, 0.125 mmol) and 5 (0.052 g, 0.125 mmol) in 10 mL of $CH_2Cl_2$ in the same conditions of the preparative reactions. After 1 h, the reaction mixture was hydrolyzed with a $NH_4Cl$ solution (25 mL, 0.1 M) extracted with $CH_2Cl_2$ (2 × 25 mL), dried over $Na_2SO_4$, and oxidized with $PbO_2$ (0.2 g) under stirring. After 0.5 h, the mixture was filtered and evaporated to dryness. The residue was added to 10 mL of DMF and 90 mL of MeOH. The obtained solution was analyzed using HPLC. (Conditions: eluant = MeOH/$H_2O$ 90:10; flow = 1.0 mL/min; temperature = 55 °C; column = Nucleosil-R C-18 5μ).

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# Photooxygenation of Silyl Ketene Acetals: Dioxetanes as Precursors to α-Silylperoxy Esters in the Silatropic Ene Reaction

Waldemar Adam* and Xiaoheng Wang

*Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-8700 Würzburg, FRG*

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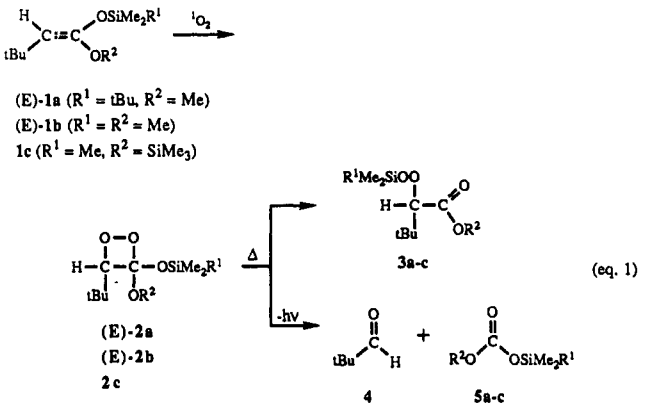
Photooxygenation of silyl ketene acetals afforded dioxetanes, which subsequently underwent secondary reactions to give rearrangement products (α-silylperoxy esters, major products) and cleavage products (pivalaldehyde, minor product). The kinetics of these reactions were studied by NMR and chemiluminescence. The activation energy of the chemiluminescent cleavage process was 2–3 kcal/mol higher than that of the rearrangement. In the presence of catalytic amounts of $CF_3COCF_3$ or $CF_3COCH_3$, the (*E*)-silyl ketene acetals rearranged into their *Z* isomers. Photooxygenation of the (*E*)- and (*Z*)-silyl ketene acetals showed that the [2 + 2] cycloaddition was rigorously diastereoselective. Trapping experiments with acetaldehyde confirmed the intermediacy of 1,4-zwitterions in the rearrangement of the (*E*)- and (*Z*)-dioxetanes into α-silylperoxy esters, but such intermediates were not detected during the photooxygenation of the silyl ketene acetals; the latter proceeds presumably via perepoxides.

The ene reaction of olefins bearing allylic hydrogens with $^1O_2$ produces allylic hydroperoxides via hydrogen migration.[1] Analogously, silyl enol ethers and ketene acetals form α-silylperoxy ketones and esters via silyl migration.[2-13] In this context, previously it was found[10] that silyl ketene acetals reacted with $^1O_2$ to give not only the expected α-silylperoxy esters, but also dioxetanes. A mechanism was proposed in which a common 1,4-dipolar intermediate served as precursor to both the dioxetanes and the silylperoxy esters. We now present evidence that esters **3** are not formed directly from the acetals **1**, but rather through rearrangement of the dioxetanes **2** (eq 1).




(eq. 1)

## Results and Discussion

*tert*-Butylketene methyl *tert*-butyldimethylsilyl acetal ((*E*)-**1a**) was prepared by the published procedure as the sole isomer, and its configuration was determined by $^1H$ NOE[14] experiments (Figure 1). The NOE spectra of the (*E*)-**1a** isomer showed a large enhancement (8%) of the olefinic proton resonance during saturation of the $SiMe_2$ group, while no corresponding effect could be observed from the methoxy group. A reverse situation was obtained for the (*Z*)-**1a** isomer, for which saturation of the methoxy group enhanced the intensity of the olefinic proton by 11%.

It was discovered that the $CF_3COCF_3$ and $CF_3COCH_3$ ketones could be used as catalysts for the geometrical isomerization of the ketene silyl acetals (*E*)-**1a,b**. When a solution of silyl ketene acetal (*E*)-**1a** was heated with catalytic amounts of $CF_3COCF_3$ or $CF_3COCH_3$ in $CCl_4$ at 35 °C and the reaction monitored by $^1H$ NMR, after several minutes the characteristic signals of (*E*)-**1a** at δ 3.51 (OMe) and 3.73 (CH) decreased and two new signals for (*Z*)-**1a** at δ 3.43 and 3.35 (ratio of integration 3:1) appeared

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