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(20) Electrolysis of equimolar amounts of **5** and **8b** at −1.3 V[9] in DMF (0.1 N $LiClO_4$, 0.05 N NH_4Br) leads to the corresponding alkyl–Co(III) complex 7**b** which was isolated and crystallized in >80% yield. Its constitution was determined by analysis ($C_{42}H_{66}BrCoN_6O_2$) and spectral data; polarography at DME in the same electrolyte shows two waves at $E_{1/2} = -1.62$ and −1.84 V.[9] Further electrolysis at −1.9 V[9] in the same electrolyte afforded >90% decalone **10b**. Thus the intermediacy of alkyl–Co(III) complexes 7 during the catalyzed reductive cyclization is clearly demonstrated. Electrolysis of **8b** at −1.9 V[8] under the same conditions but in the absence of **4** or **5** shows no conversion; at a more negative potential (−2.4 V[9]) a mixture of several organic compounds as well as organomercurials was formed, but decalone **10b** could not be detected.
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(22) 7 easily exchanges the axial ligand Y. $E_{1/2}(1)$ of 7 (determined by CV in DMF, TAAP): −1.38 (R = CH_3; Y = ClO_4); −1.44 (R = CH_3; Y = Br); −1.72 V[9] (R = CH_3; Y = CN).
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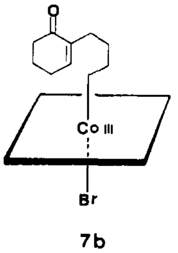

7b

Rolf Scheffold,* Meera Dike, Suneel Dike
Thomas Herold, Lorenz Walder
Institute of Organic Chemistry, University of Berne
Freiestrasse 3, CH-3012 Berne, Switzerland

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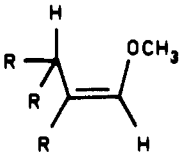
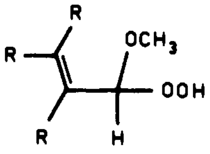
Formation of 1,2-Dioxetanes and Probable Trapping of an Intermediate in the Reactions of Some Enol Ethers with Singlet Oxygen

Sir:

Practical as well as theoretical interest accrues to methods for diverting the "ene reaction" of alkenes with singlet oxygen to a cycloaddition pathway. This goal is usually reached either by using alkenes devoid of allylic hydrogens or by circumventing by steric strain[1] the allylic shift ubiquitous to the ene reaction.[2] Enol ethers (**1**) bearing an allylic hydrogen atom also undergo dye sensitized photooxygenation to give hydroperoxides (**2**).[3] However, for enol ethers it is known that product distributions also respond to solvent polarity,[3d,e] which fact might open a general route to 1,2-dioxetanes (**3**). With this knowledge in mind, coupled with the general and qualitative observation that 1,2-dioxetanes incorporating carbocyclic rings, especially six-membered, often have good stability, the effect of changing some experimental parameters on the reactions of **1a–c** was examined.



1



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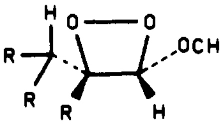

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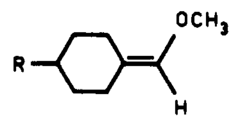
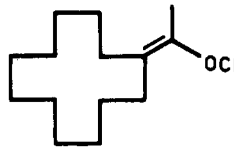


1a: R = H
1b: R = $(CH_3)_3C$



1c

The effect of changing solvent *and temperature* on the photooxygenations of **1a–c** is shown in Table I. As reported,[3a] photooxygenation of **1a** in C_6H_6 at room temperature affords virtually exclusively **2a.** However, on changing the solvent to CH_2Cl_2 27% **3a** is formed and this becomes the major product on lowering the temperature or using CH_3OH as solvent (but

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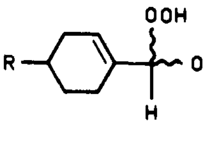
Table I. Effect of Solvent ad Temperature on the Product Distributions from Enol Ethers **1a–c**[a]

enol ether (**1**)	solvent	temp, °C	ene product (**2**),[b] %	1,2-dioxetane (**3**),[b]
1a	C_6H_6	20	97	3
1a	CH_2Cl_2	20	73	27
1a	CH_2Cl_2	−80	35	65
1a	$CH_3O_2CCH_3$[c]	−75	50	50
1a	CH_3OH[d]	20	32	48
1a	CH_3OH[d]	−80	9	54
1b	C_6H_6	20	97[e]	3[f]
1b	CH_2Cl_2	20	79[e]	21[f]
1b	CH_2Cl_2	−80	40[e]	60[f]
1c	C_6H_6	20	99[g]	1
1c	CH_2Cl_2	20	92[g]	8
1c	CH_2Cl_2	−80	61[g]	39

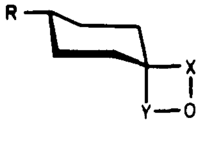
[a] Tetraphenylporphine (~10^{-4} M) sensitized photooxygenation using $K_2Cr_2O_7$ in H_2O as filter; room temperature reactions were carried out at 1.7–10^{-2} M and low temperature reactions at 10^{-2} M concentrations. [b] Yields were determined by ^{1}H NMR (60 MHz). [c] Reaction was very sluggish; Rose Bengal and tetraphenylporphine were used as dyes. [d] See discussion in text concerning material balances; Rose Bengal was used as sensitizer. [e] Two *dl* pairs. [f] Two geometrical isomers; see text. [g] The *E* and *Z* isomers were present in an ~1:1 ratio.

see below). The same trend is clearly seen with **1b,c** (Table I).



2a; R = H

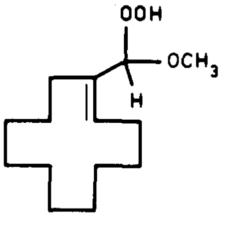
2b,b′; R = $(CH_3)_3C$



3a; R = H, X = $CHOCH_3$, Y = O

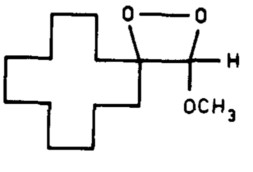
3b; R = $(CH_3)_3C$, X = O, Y = $CHOCH_3$

3b′; R = $(CH_3)_3C$, X = $CHOCH_3$, Y = O



2c

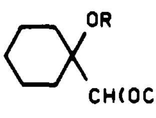
2c′ (*E*-isomer)



3c

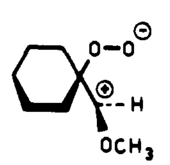
The dioxetanes **3b,b′** (see below for stereochemistry) are stable for long periods at room temperature, whereas **3a** and **3c** undergo slow (hours) decomposition at 30 °C but are entirely stable at 0 °C or lower. The dioxetanes were identified by their ^{1}H NMR and ^{13}C NMR spectra[4] and their thermal (60–70 °C) decomposition with chemiluminescence to methyl formate and the respective ketones. Further structural confirmation and stereochemical assignments were made by reducing the crude reaction mixtures with $NaBH_4$ in CH_3OH; this leads cleanly to allylic alcohols from **2** and 1,2-glycols from **3**. Yields and recovery of products were nearly quantitative. The glycols were prepared for comparison purposes by OsO_4 hydroxylation of the appropriate methylenecycloalkanes.

When the photooxygenation of **1a** was carried out in CH_3OH at ambient temperature (Table I), in addition to the absorptions for **2a** and **3a**, new peaks, subsequently assigned to **4** (20%), appeared in the NMR spectra. At −80 °C in CH_3OH the ene reaction was nearly suppressed (9%) and the yield of the new product was increased to 37%. On the basis of spectral data and quantitative reduction by $NaBH_4$ in CH_3OH to **5**,[5] prepared independently by acid-catalyzed addition of CH_3OH to 1-hydroxycyclohexanecarboxyaldehyde,[6] the new product was assigned structure **4**.

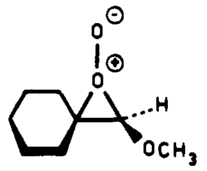


4: R = OH

5: R = H



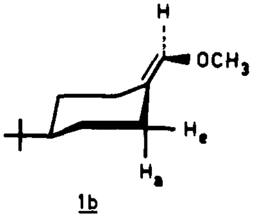
6



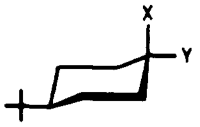
7

The formation of **4** (trapping experiments with other compounds have not yet been carried out) is most easily, but not necessarily uniquely, rationalized by assuming addition of CH_3OH to dipolar ion **6** or perhaps perepoxide **7**. (Methanol does not add to **3a**.) Note that **6** cannot in any obvious fashion be a precursor of ene product **2a** except that **6** rearranges to **7** or to the other dipolar ion structure with a tertiary carbonium ion center, not shown. The latter type of dipolar ion[7] (or biradical)[7d] has been repeatedly suggested as an intermediate in the ene reaction, although the suggestion has not been universally accepted.[8] 2-Methoxynorbornene, which cannot undergo the ene reaction, is reported to afford a trapping product structurally analogous to **4**.[7b,c]

The stereochemistry of 1,2-dioxetane formation was examined with conformationally fixed **1b**. If the requirement in the ene reaction for an allylic hydrogen parallel to the π system is absolute,[2] and if the reaction is suprafacial,[9] one anticipates, but cannot prove with **1b**, that H_a rather than H_e should be abstracted (see drawing). Of special—and testable—interest is whether 1,2-dioxetane formation with **1b** occurs preferably on the side of the double bond not possessing a properly aligned allylic hydrogen, i.e., cis to the $(CH_3)_3C$ group (**3b′** as major product).



1b



8: X = OH, Y = CH_2OH

9: X = CH_2OH, Y = OH

The crude reaction mixture obtained on photooxygenation of **1b** (CH_2Cl_2, −80 °C) contains *two* 1,2-dioxetanes (combined yield 60%) as determined from ^{1}H NMR absorptions for -C*H*(OCH_3)O at δ 5.11 and 5.14 (C_6D_6). The crude reaction mixture was reduced with $NaBH_4$ in CH_3OH and was shown to consist of both glycols **8** and **9** present in roughly equal amounts and allylic alcohol.[10,11] A conservative interpretation of this observation is that cycloaddition to form 1,2-dioxetane, even in the face of an ideal steric situation for the ene reaction (trans face of double bond in **1b**), competes effectively (i.e., **9** derived from "unexpected" product **3b** is also formed) under the proper experimental conditions. We have reported previously stereochemical peculiarities of the ene reaction using conformationally fixed alkenes.[12]

In summary, increased solvent polarity and/or lower temperatures favor 1,2-dioxetane formation from enol ethers at the expense of ene-reaction products, an intermediate in the photooxygenation of enol ethers appears to have been trapped, and an intriguing stereochemical point has been brought to light.

Acknowledgment. We are grateful to Dr. P. M. Collins, Birbeck College, for sending us information on the NMR spectra of **8** and **9**. Mr. W. H. Kruizinga provided synthetic assistance at various stages.

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(4) For example the presence and amount of **3a** is readily established from its characteristic absorption (C_6D_6) at δ 5.08 (s, 1, $-OOCH(OCH_3)$) and 3.00 (s, 3, OCH_3) and partial ^{13}C NMR ($CDCl_3$, relative to Me_4Si) at δ 109.0 (d, $J = 177$ Hz, $OOCH(OCH_3)$) and 89.5 (s, quarternary C). The allylic alcohol from **2a** and glycol from **3a** (as well as from the other products reported here) were fully characterized by spectral data and comparison with authentic samples.

(5) Partial NMR of **4**: ^1H (C_6D_6) δ 4.15 (s, 1, $CH(OCH_3)_2$) and 3.23 (s, 6, OCH_3); ^{13}C ($CDCl_3$), δ 58.0 (q, $J = 166$ Hz, OCH_3), 83.4 (s, quaternary C), and 108.4 (d, $J = 130$ Hz, $CH(OCH_3)_2$). Note that the *hemiacetal* group of **2** on reduction under basic conditions reduces to alcohol. The *acetal* group of **4** will not reduce under these conditions. The product **5** was identical in all respects with authentic material.[6]

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(9) However, see the discussion by A. A. Frimer, *Chem. Rev.*, **79**, 359 (1979).

(10) The stereochemistries of **8** and **9** have been established and the ^{13}C NMR shifts for each carbon atom of the ring and the CH_2OH have been assigned.[11] In the product mixture resulting on reduction, the absorptions for four of the ring carbons and the CH_2OH did not overlap with those of the allylic alcohol and could be assigned. Observed ^{13}C NMR shifts (literature[11] values in parentheses): for **8**, δ 65.6 (65.7) (CH_2OH), 72.3 (72.6) (quaternary C), 35.3 (35.4) ($-CH_2C(OH)CH_2OH$), and 47.4 (47.5) (tertiary C); for **9**, δ 71.8 (71.8) (CH_2OH), 71.0 (71.2) (quaternary C), 34.0 (34.2) ($-CH_2C(OH)CH_2OH$), and 48.1 (48.2) (tertiary C). The presence of **8** and **9** was further ascertained by comparison with authentic samples.

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E. W. H. Asveld, Richard M. Kellogg*
Department of Organic Chemistry
University of Groningen, Nijenborgh
Groningen 9747 AG, The Netherlands

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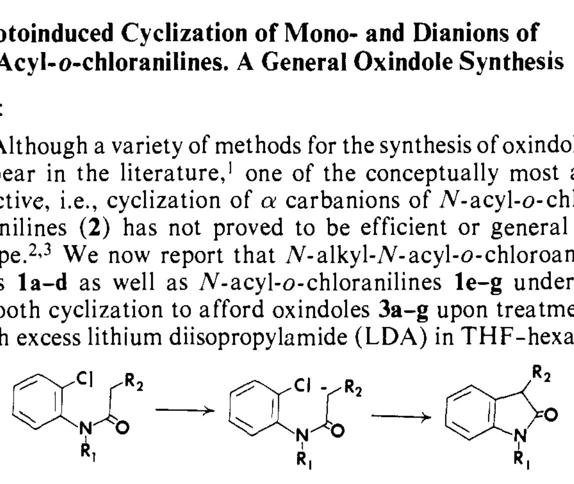
Photoinduced Cyclization of Mono- and Dianions of *N*-Acyl-*o*-chloranilines. A General Oxindole Synthesis

Sir:

Although a variety of methods for the synthesis of oxindoles appear in the literature,[1] one of the conceptually most attractive, i.e., cyclization of α carbanions of *N*-acyl-*o*-chloroanilines (**2**) has not proved to be efficient or general in scope.[2,3] We now report that *N*-alkyl-*N*-acyl-*o*-chloroanilines **1a–d** as well as *N*-acyl-*o*-chloranilines **1e–g** undergo smooth cyclization to afford oxindoles **3a–g** upon treatment with excess lithium diisopropylamide (LDA) in THF-hexane followed by near-UV irradiation of the resulting monoanions **2a–d** ($R_1 = CH_3$, $C_6H_5CH_2$) and dianions **2e–g** (R_1 = Li).



1a-g **2a-g** **3a-g**

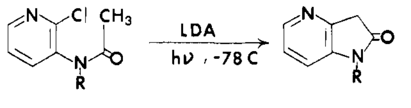
Table 1. Photoinduced Cyclization of *N*-Acyl-*o*-chloranilines **1** to Form Oxindoles **3**

starting anilide no.	starting anilide R_1	starting anilide R_2	product no.[a]	isolated yield, %[b]
1a	CH_3	C_6H_5	**3a**[c]	64
1b	CH_3	H	**3b**[c]	82
1c	CH_3	*n*-C_4H_9	**3c**[d]	73
1d	$C_6H_5CH_2$	H	**3d**[e,f]	32[g]
1e	H	C_6H_5	**3e**[h]	63
1f	H	H	**3f**[i]	74
1g	H	CH_3	**3g**[j]	73

[a] ^1H NMR spectra of all products were consistent with assigned structures. Physical constants of known compounds were in agreement with published values. [b] Unless noted otherwise, irradiation was conducted for 3 h. [c] Reference 3. [d] Daisley, R. W.; Walker, J. *J. Chem. Soc. C* **1971**, 1375. [e] Satisfactory elemental analysis was obtained for this compound. [f] Yield was determined by GC. [g] Irradiated for 0.5 h. [h] Bruce, J. M.; Sutcliffe, F. K. *J. Chem. Soc.* **1957**, 4789. [i] Bayer, A. *Ber.* **1878**, *11*, 583. [j] Reference 8.

Results of a representative series of reactions are presented in Table I, where it may be seen that this mild procedure affords generally good yields of oxindoles with various alkyl substitution patterns at positions 1 and 3. Comparison of these results with those of earlier efforts[3] to effect cyclization of anilides **1b**, **1e**, and **1f** through intramolecular addition of the laterial carbanions to an aryne intermediate clearly demonstrates the advantages of the photostimulated process. Moreover, the present method provides a route to oxindoles from anilides which cannot be converted into the required arynes because of substituents flanking the halogen of the benzene ring (vida infra).

2-Chloro-3-(*N*-methylacetamido)pyridine (**4a**) also underwent photocyclization to afford azaoxindole[4] **5a** (83%). In this case it was necessary to maintain the reaction mixture at −78 °C to prevent decomposition of the intermediate carbanion. Interestingly, the unmethylated pyridine **4b** was not converted into the expected **5b** under similar conditions. Instead, **4b** was recovered.



4a, R = CH_3
b, R = H

5a, R = CH_3
b, R = H

Photocyclization of **1d** with KNH_2 in liquid NH_3 afforded 57% oxindole **3d** along with 8% aryne-derived *N*-benzyl-*m*-aminoacetanilide. Attempted cyclizations of **1b** and **1f** under similar conditions led to much lower yields of the desired oxindoles than obtained with LDA.

Preliminary mechanistic studies with **1d** and **1f** reveal that the LDA-mediated reactions involve initial side-chain carbanion formation, but do not proceed via nucleophilic addition to an aryne intermediate. Thus, reaction of **1d** and **1f** with excess LDA in THF without illumination, followed by quenching with D_2O, resulted in quantitative recovery of starting materials containing >0.95 deuterium atom (^1H NMR) in the respective acetyl methyl group. Isolation of oxindoles **7a**[4] (87%) and **7b**[5] (76%) from 3-substituted 2-chloroanilides **6a** and **6b**, respectively, rule out an aryne mechanism. The requirement for Pyrex-filtered light and the inhibitory action of di-*tert*-butyl nitroxide indicate that the present reactions may represent one of the few reported examples of an intramolecular $S_{RN}1$ mechanism.[6,7] Additional studies concerning the mechanistic details of these reactions are in progress.