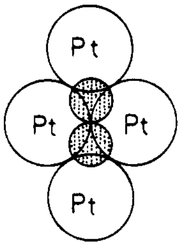
with 0.98 Å longer Ni_b–Ni_b and 0.036 Å longer Ni_a–Ni_b separations. Whereas the shape of the $Ni_4[CNC(CH_3)_3]_4[\mu_3(\eta^2)\text{-}C_6H_5C{\equiv}CC_6H_5]_3$ molecule is reasonably equidimensional, the $Ni_4[CNC(CH_3)_3]_7$ molecule is much more disk shaped with the trigonally expanded $Ni_bNi_bNi_b$ basal face much more exposed. The isocyanide ligands in **2** appear to be able to span the elongated Ni_b–Ni_b edges quite effectively by simply changing the hybridization of their Ni_b-bonded nitrogens from sp to sp^2 and directing C_1 toward the other basal nickel atom to give bent, "edge-bridging" isocyanide ligands but similar "edge-bridging" acetylenes would probably produce unfavorable steric interactions.

Hydrogen reacted with **1** in a toluene solution at 25° to yield *cis*-$(C_6H_5)CH{=}CH(C_6H_5)$, isocyanide, and nickel metal. A fully analogous reaction with the 3-hexyne cluster was observed; *cis*-3-hexene and isocyanide were the only organic products detected. Addition of excess acetylene to these reaction systems fully suppressed nickel metal formation, and a catalytic reduction of the acetylene to the cis olefin[13] was observed. In sharp contrast, the mononuclear complex $[(CH_3)_3CNC]_2Ni(C_6H_5C{\equiv}CC_6H_5)$ did not react with hydrogen at 25° within a period of 2 days. These data would seem to provide a qualitative argument in support of cluster catalysis at least for acetylene reduction as differentiated from an alternative mechanistic mode which comprises cluster fragmentation to mononuclear intermediates.[13,14] Characterization of presumed hydride intermediates is now being attempted.

A dihapto binding of CO was earlier proposed[1] by us as a possible feature in the hydrogen reduction of carbon monoxide with metal cluster catalysts. With the demonstration of this feature in acetylene reductions, we now suggest that this concept can be extended to other important catalytic reactions in which triple bonds are hydrogenated, e.g., the hydrogen reduction of dinitrogen, since the bond order of the triple bond is substantially reduced in this type of cluster bonding. By our analogy,[6] $\mu_x(\eta^2)$-bonding modes for molecules with triple bonds could be important in reaction intermediates for catalytic reactions on metal surfaces. Somorjai and co-workers[15] present evidence that acetylene on a platinum(111) surface is largely as shown in **3** with about a 1.34 Å C–C separation.



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This type of interaction has a formal resemblance to the acetylene interaction in the nickel cluster.[16]

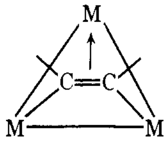
Acknowledgment. Support of this research by the Advanced Research Projects Agency, Cornell Materials Science Center, by the National Science Foundation, Grant No. GP-39306X (E.L.M.), and the donors of the Petroleum Research Fund, administered by the American Chemical Society (V.W.D.), is gratefully acknowledged.

References and Notes

(1) Paper 4, M. G. Thomas, B. F. Beier, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1296 (1976).

(2) A fully analogous and the first reported example of this acetylene subclass is $Ni_4(CO)_4[\mu_3(\eta^2)\text{-}CF_3C{\equiv}CCF_3]_3$, a relatively unstable cluster molecule. J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J. Am. Chem. Soc.*, **97**, 7492 (1975).

(3) (a) A full characterization of this type of ligand interaction as "4-electron" requires a substantial reduction of the bond order (acetylene or isocyanide bond). Actually, the observed C–C and C–N bond distances for the bridging ligands in these clusters[2,4] are close to a double or aromatic bond value. We purposely employ this terminology to emphasize the potential of such interaction modes in the ground or excited states in the reduction of the bridging bonds. (b) The $\mu_3(\eta^2)$ notation is incomplete and would not discriminate between the interaction of acetylene in this cluster and an alternative arrangement of the type



A discrimination could be achieved by the notations $\mu_3(\eta^2{}_\perp)$ and $\mu_3(\eta^2{}_\parallel)$ for the two respective cases but we hesitate to introduce new connexity notations until this problem has been more carefully considered. (The μ_x notation is taken here to simply represent the number (x) of metal atoms bridged by the ligand.)

(4) V. W. Day, R. O. Day, J. S. Kristoff, F. J. Hirsekorn, and E. L. Muetterties, *J. Am. Chem. Soc.*, **97**, 2571 (1975).

(5) M. G. Thomas, B. F. Beier, and E. L. Muetterties, manuscript in preparation.

(6) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975).

(7) The cluster is insoluble in pentane but dissolves in this medium if 1 mol of an acetylene, such as 2-butyne or phenylacetylene, per mole of cluster is added.

(8) Spectroscopic studies showed no evidence of cluster fragmentation. NMR studies established that the cluster is intact although the ligand resonances are significantly shifted from those for the ligands of the cluster (dissolved in benzene). A more complete discussion of these complexes will be given elsewhere.[5]

(9) Elemental analysis, all elements, were in full agreement with the calculated percentages for the complex which was crystallized from pentane. The crystal used in the x-ray study was selected from a set obtained by recrystallization from a benzene–pentane mixture and retained benzene of solvation.

(10) The four crystallographically independent nickel atoms were located through direct methods and the remaining non-hydrogen atoms of the totally general position asymmetric unit were located by standard difference Fourier techniques. Further refinement is underway.

(11) J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hubel, *J. Am. Chem. Soc.*, **88**, 292 (1966).

(12) The first number in parentheses is the root mean square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the average value, respectively. Full structural data will be published shortly.

(13) The critical test of catalyst selectivity in the acetylene reduction will be the hydrogenation of $C_6H_5C{\equiv}CD$. We also plan to explore similar catalytic reactions of other $\mu_x(\eta^2)$-acetylene dinuclear, trinuclear, and tetranuclear metal complexes to establish the general importance of $\mu_x(\eta^2)$-acetylene bonds in catalysis.

(14) A solely cluster based catalytic cycle can never be definitively proven; it can only be *definitively* disproven.

(15) Personal communication from Professor Somorjai. L. L. Kesmodel, P. C. Stair, and G. A. Somorjai, to be published in *Phys. Rev. Lett.*

(16) This is more nearly analogous to the μ_4 binding of $C_6H_5C{\equiv}CC_6H_5$ in $Co_4(CO)_{10}(C_6H_5C{\equiv}CC_6H_5)$ although the C—C bond distance is much longer (1.44 Å) in the cluster (L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.*, **84**, 2450 (1965)). In the $\mu_2(\eta^2)$-binding of acetylenes in $Co_2(CO)_6(RC{\equiv}CR)$ complexes, the C—C separation is 1.32–1.37 Å (R. S. Dickson and P. J. Fraser, *J. Organomet. Chem.*, **12**, 323 (1974)) and is 1.35 Å in $(C_5H_5)_2Ni_2(RC{\equiv}CR)$, (O. S. Mills and B. W. Shaw, *J. Organomet. Chem.*, **11**, 595 (1968)). In the μ_3-η^2 binding of diphenylacetylene in $Fe_3(CO)_9(RC{\equiv}CR)$, the C—C separation is 1.41 Å,[10] and in $Fe_2(CO)_6[(CH_3)_3CC{\equiv}CC(CH_3)_3]$ the C—C separation is 1.32 Å (F. A. Cotton, J. D. Jamerson, and B. R. Stults, *J. Organomet. Chem.*, **94**, C53 (1975)).

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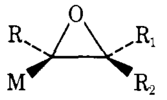
Feasible Route to 1,2-Epoxyalkyllithium Reagents via the Lithiation of Epoxyethylsilanes[1]

Sir:

The availability of an α-metalated epoxide synthon (**1**) would be most useful in organic synthesis, for such a unit



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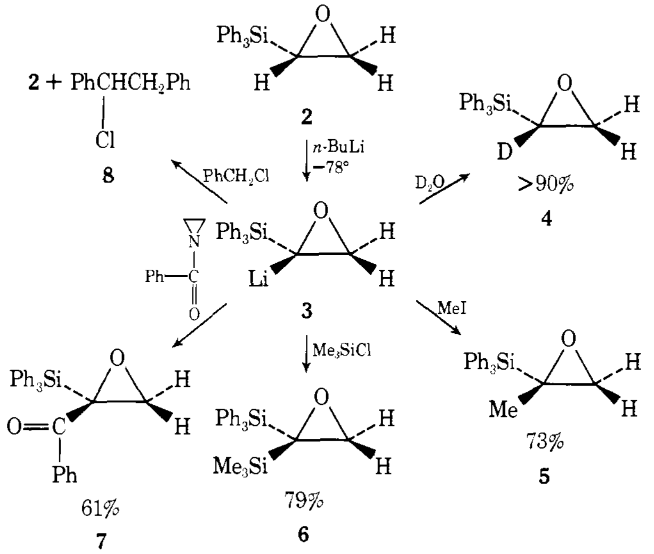
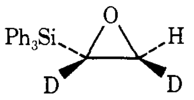
constitutes a valuable precursor to carbonyl, glycolic, and hydroxyalkyl functions,[2] as well as a fragment bearing two carbon centers of defined chirality.[3] Despite their great potential in synthesis, up to the present metalated epoxides have not been prepared in any practical manner and have only been detected as transient intermediates in the reactions of strong bases with epoxides.[4] During a study of the reactions of organolithium reagents with epoxyalkylsilanes[1] we found that at −78° *n*-butyllithium in tetrahydrofuran was able to metalate epoxyethyltriphenylsilane (**2**) in high yield and exclusively on the epoxide carbon *α* to silicon. The resulting 1-triphenylsilyl-1,2-epoxyethyllithium (**3**) was found to retain its stereochemical and structural integrity at this temperature, and it could be quenched with various reagents to form epoxide derivatives of **2** in high yields (Scheme I).

Scheme I



Thus, when 4.8 mmol of *n*-butyllithium (in a 2.4 M hexane solution) were added to 1.0 mmol of **2** in 10 ml of anhydrous tetrahydrofuran at −78° and the solution allowed to stir for 4 h at −78°, a quench with D_2O (99.8%) and workup gave 1-deuterioepoxyethyltriphenylsilane (**4**) in >90% yield, which by NMR spectroscopy was 100% deuterated at C_1. Similar reaction mixtures of **3** were treated with various reagents to give high yields of isolated derivatives: (a) methyl iodide:2-(1,2-epoxypropyl)triphenylsilane (**5**, 73%); (b) chloro(trimethyl)silane:1-trimethylsilyl-1-triphenylsilylepoxyethane (**6**, 79%); and (c) *N*-benzoylaziridine:1-benzoylepoxyethyltriphenylsilane (**7**, 61%). With benzyl chloride and **3** hydrogen-lithium exchange apparently occurred preferentially, for much *α*-chlorobibenzyl (**8**) was detected and the starting expoxide recovered.

The configurational stability of the 1-triphenylsilyl-1,2-epoxyethyllithium system (**3**) was assessed by treating *cis*-1,2-dideuterioepoxyethyltriphenylsilane (**9**)[1] with *n*-butyllithium at −78° and then quenching with H_2O. The isolated 2-deuterioepoxyethyltriphenylsilane (**11**) was shown by NMR spectroscopy to have the trans configuration (**2** NMR (CCl_4) 2.45 (d of d, *β*-cis H, $J_{\mathrm{gem}} = 5.5$ Hz and $J_{\mathrm{trans}} = 4.2$ Hz; 2.85) (m, *α*- and *β*-trans H); **11** 2.45 (m of width = 4 Hz), 1 H; 2.85 (d, $J_{\mathrm{trans}} = 4.2$ Hz), 1 H).



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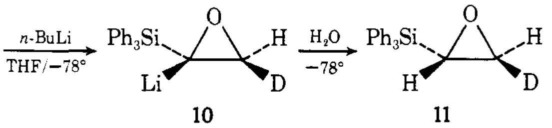
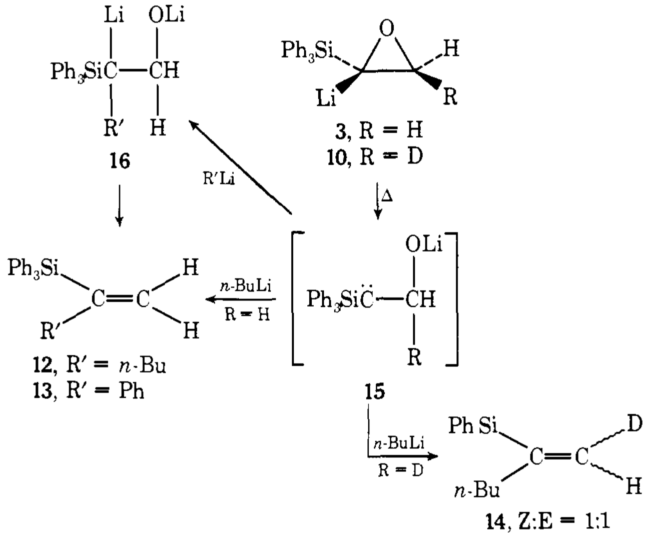
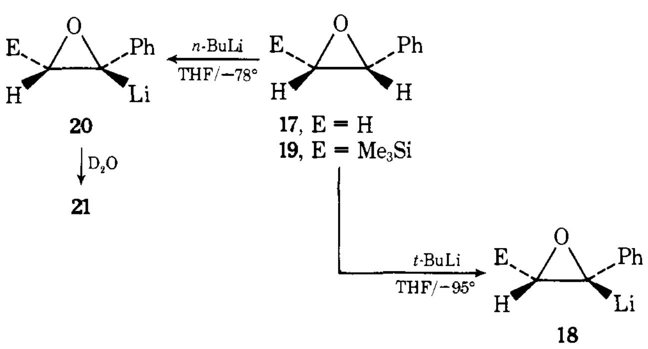


Since the lithium reagent **3** could be a potential carbenoid source, via *α*-elimination,[4] an attempt to trap such a carbenoid was undertaken. Thus, **3** was generated in the presence of excess *n*-butyllithium and the solution allowed to warm to 25°. Hydrolytic workup yielded 70% of 1-hexen-2-yl(triphenyl)silane (**12**). Alternatively, when **3** was formed from the action of 1 equiv of *n*-butyllithium on **2** and then an excess of phenyllithium was added, workup yielded 66% of triphenyl(*α*-styryl)silane (**13**).[5] Finally, as a probe of stereochemistry, **9** was treated with excess *n*-butyllithium to form **10** and then **10** was allowed to react with the remaining *n*-butyllithium. The deuterated **12** was shown to be a 1:1 mixture of (*Z*)- and (*E*)-*β*-deuterio isomers (**14**) (Scheme II). These results support a mechanistic pathway whereby **3** undergoes an *α*-elimination to yield carbenoid **15**, which is captured by R′Li to form intermediates like **16**, which in turn can undergo readily the loss of lithium oxide.[6] The nonstereoselective capture of *n*-BuLi by **15** (R = D) would nicely explain the 1:1 mixture (*Z*)- and (*E*)-*β*-deuterio-**14**.

Scheme II



The aforementioned metalation of epoxides does not require the presence of an *α*-substituted silyl group. Styrene oxide (**17**) was found to be metalated exclusively at the carbon *α* to the phenyl group (**18**) by either *n*-butyl- or *tert*-butyllithium in THF at −78 or −95°, respectively. By quenching such reactions with D_2O, the amount of metalation approached 50%, although the recovery of **17** was only ca. 50%. The presence of



a β-trimethylsilyl in **17**, however, did enhance the ease of metalation, as well as the kinetic stability of the α-lithioepoxide, even though metalation occurred α to phenyl. Thus, β-trimethylsilylstyrene oxide (**19**) underwent metalation with *n*-butyllithium at −78° to yield **20**, which upon treatment with D_2O provided a high yield of configurationally unchanged **18** completely α-deuterated (**21**).

These metalation studies are being extended to other silylepoxides (**1**, R = R_3Si and R_1,R_2 = H, alkyl) and ordinary epoxides (**1**, R,R_1,R_2 = H or alkyl) as a means of developing practical nucleophilic epoxide synthons.[7] It should be noted that previous work with epoxyalkylsilanes has already established such systems as attractive precursors to silicon-free carbonyl, olefinic, or hydroxylic derivatives.[8] Further developments on such silylepoxide chemistry are receiving our earnest attention and some of these will be published shortly.[1]

Acknowledgments. The authors are indebted to the National Cancer Institute of the Public Health Service for support of this research under Grant CA-14540.

References and Notes

(1) Part 14 of the series, "Organosilicon Compounds with Functional Groups Proximate to Silicon"; for the previous part, cf. J. J. Eisch and J. E. Galle, *J. Org. Chem.*, in press.

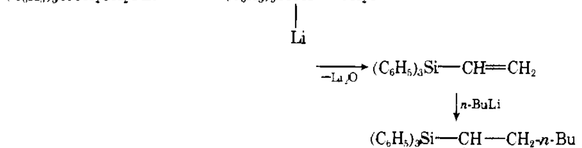
(2) Cf. J. E. Baldwin, Jr., G. A. Höfle, and O. W. Lever, Jr., *J. Am. Chem. Soc.*, **96**, 7125 (1974), for the use of metalated enol ethers as reagents for nucleophilic acylation and for extensive leading references to synthetic equivalents of the acyl anion.

(3) For reviews of the chemical transformations of epoxides and the attendant stereochemistry, cf. (a) H. C. van der Plas, "Ring Transformations of Heterocycles", Vol. 1, Academic Press, New York, N.Y., 1973, pp 2–41; (b) S. Patai, Ed., "The Chemistry of the Ether Linkage", Interscience, New York, N.Y., 1967; (c) M. S. Malinovskii, "Epoxides and their Derivatives", translated from the 1961 Russian edition, Sivan Press, Jerusalem, 1965; (d) R. E. Parker and N. S. Isaac, *Chem. Rev.*, **59**, 737 (1959); and (e) S. Winstein and R. B. Henderson in "Heterocyclic Compounds", Vol. 1, R. C. Elderfield, Ed., Wiley, New York, N.Y., 1950, pp 1–60.

(4) Cf. inter alios: (a) A. C. Cope, H. H. Lee, and H. E. Petree, *J. Am. Chem. Soc.*, **80**, 2849 (1958); (b) A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *ibid.*, **82**, 6370 (1960); (c) J. K. Crandall and L.-H. C. Lin, *J. Org. Chem.*, **33**, 2375 (1968), and references cited therein; (d) R. P. Thummel and B. Rickborn, *ibid.*, **37**, 4250 (1972), and references cited therein.

(5) When **2** is treated with an excess of phenyllithium in ethyl ether solution, an entirely different reaction ensues, leading to styrene and tetraphenylsilane. Treatment of 1-deuterio-1,2-epoxyethyltriphenylsilane with phenyllithium yields styrene exclusively deuterated on its α-carbon. Finally, use of **9** in such a reaction gives a 1:1 mixture of (*Z*)- and (*E*)-α,β-dideuteriostyrene. All these results are consistent with the direct attack of phenyllithium on silicon in **2** to form tetraphenylsilane and the transient epoxyethyllithium (cf. ref 1).

(6) (a) J. K. Crandall and L.-H. C. Liu, *J. Am. Chem. Soc.*, **89**, 4526, 4527 (1967), have proposed the formation of such epoxide ions and carbenoids as fleeting intermediates in the reactions of *tert*-butyllithium with epoxides. Furthermore, they have persuasively advocated the importance of lithium oxide eliminations in such processes. (b) The formation of 1-trimethylsilyl-1-*tert*-butylethylene from epoxyethyltrimethylsilane and *tert*-butyllithium, briefly mentioned in ref 8c, could result either from a sequence of steps similar to **2** → **15** → **16** → **12** or from opening of the epoxide ring at C_1 by *tert*-butyllithium, followed by metalation at C_1 and the elimination of Li_2O. As to the latter possibility, we have found that 2-triphenylsilylethanol reacts with an excess of *n*-butyllithium to yield *n*-hexyl(triphenyl)silane. The pathway indicated is therefore:



$$(C_6H_5)_3SiCH_2CH_2OLi \xrightarrow{n\text{-BuLi}} (C_6H_5)_3Si\underset{\substack{|\\ Li}}{CH}-CH_2OLi \xrightarrow[-Li_2O]{} (C_6H_5)_3Si-CH=CH_2 \xrightarrow{n\text{-BuLi}} (C_6H_5)_3Si-\underset{\substack{|\\ Li}}{CH}-CH_2\text{-}n\text{-}Bu$$

The choice between the carbenoid pathway vs. the epoxide ring-opening and elimination pathway for the formation of 1-trimethylsilyl-1-*tert*-butylethylene could only be reached by deuterium-labeling studies, as was done here with **10**. The carbenoid pathway would involve nonstereospecific olefin formation, whereas an epoxide opening-elimination process would be expected to be stereospecific (ref 1).

(7) By use of *n*-butyl- or *tert*-butyllithium at temperatures between −75° and −110° in ethyl ether–hexane–tetrahydrofuran mixtures, the following epoxides have been metalated: (a) *trans*-1,2-epoxyoct-1-yl(triphenyl)silane at C_1 (**1**: R = $(C_6H_5)_3Si$; R_1 = H; R_2 = *n*-C_6H_{13}; M = Li); (b) *trans*-2-benzenesulfonyl-1,2-epoxy-1-phenylethane at C_2 (**1**: R = $C_6H_5SO_2$; R_1 = H; R_2 = C_6H_5; M = Li); and (c) 2,3-epoxy-3-methylbutanenitrile at C_2 (**1** R = CN; R_1 and R_2 = CH_3; M = Li). The success of the metalation was discerned by treating **1** with D_2O or $(CH_3)_3SiCl$ and isolating the labeled epoxide. Preliminary studies have also shown that epoxycycloalkanes and trimethylsilyl-substituted epoxides can be metalated, but, thus far, the recovery of epoxide has not been satisfactory.

(8) Cf. ref 1 for leading references to the use of organosilicon derivatives in organic synthesis; also, for key references on silyl epoxides, cf. (a) J. J. Eisch and J. T. Trainor, *J. Org. Chem.*, **28**, 2870 (1963); (b) G. Stork and M. E. Jung, *J. Am. Chem. Soc.*, **96**, 3682 (1974); (c) R. K. Boeckman, Jr., and K. J. Bruza, *Tetrahedron Lett.*, 3365 (1974); (d) T. H. Chan, M. P. Li, W. Mychajlowskij, and D. N. Harpp, *Tetrahedron Lett.*, 3511 (1974); and (e) P. F. Hudrlik, D. Peterson, and R. J. Rona, *J. Org. Chem.*, **40**, 2263 (1975).

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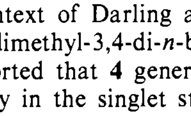
Tetraethyldioxetane and 3,4-Dimethyl-3,4-di-*n*-butyl-1,2-dioxetane. High Ratio of Triplet to Singlet Excited Products from the Thermolysis of Both Dioxetanes

Sir:

The thermolysis of dioxetanes is now an established source of excited carbonyls.[1] It is likely that the effect of structural changes will help elucidate the still-debated mechanism of this reaction. For example, tetramethoxydioxetane (**1**) was found to be considerably more stable than tetramethyldioxetane (**2**) and to give fewer excited products.[2] To understand this particular substituent effect, tetraethyldioxetane (**3**) was now synthesized, in which the ethyl groups can be regarded as models, from the steric viewpoint, for the methoxy groups of **1**. **3** is interesting also in the context of Darling and Foote's unexpected results with 3,4-dimethyl-3,4-di-*n*-butyldioxetane (**4**).[3] These authors reported that **4** generates little excited ketone, predominantly in the singlet state ($^3\phi = 0.035$, $^1\phi = 0.05$), basing their determination of excitation yields on type II processes (elimination and cyclization) from excited 2-hexanone. Since **3** was found to give a high yield of triplet products and few excited singlets, like **2**, **4** was reinvestigated by the same luminescence techniques[4] and found, in fact, to show the same preference for triplet products, like all *isolated* dioxetanes for which this information is now available.[1c] In retrospect, it would be difficult to rationalize how the length of the butyl groups could cause drastic differences between the excitation yields of **3** and **4**.



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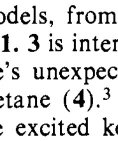

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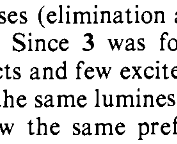

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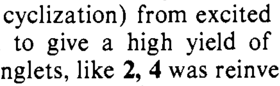

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The thermolyses of dioxetanes **3** and **4**[5] produce 3-pentanone and 2-hexanone as only products detected by NMR and are accompanied, in aerated benzene or xylenes, by weak chemiluminescences, which are strongly enhanced by the addition of 9,10-dibromoanthracene (DBA) or 9,10-diphenylanthracene (DPA). The decay of chemiluminescence follows a strict first-order course independent of fluorescer.