

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

- 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.
- 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.
- 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. Malinowski, "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. Weinstein and R. B. Henderson in "Heterocyclic Compounds", Vol. 1, R. C. Elderfield, Ed., Wiley, New York, N.Y., 1950, pp 1-60.
- 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. Liu, *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.
- 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 epoxyethylolithium (cf. ref 1).
- (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** \rightarrow **15** \rightarrow **16** \rightarrow **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:

$$(C_6H_5)_3SiCH_2CH_2OLi \xrightarrow{n-BuLi} (C_6H_5)_3SiCH(Li)CH_2OLi$$

$$\xrightarrow{-Li_2O} (C_6H_5)_3Si-CH=CH_2$$

$$\downarrow n-BuLi$$

$$(C_6H_5)_3Si-CH(Li)-CH_2-n-Bu$$
- 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).
- 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.
- 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. Mychajlowski, and D. N. Harpp, *Tetrahedron Lett.*, 3511 (1974); and (e) P. F. Hudrik, D. Peterson, and R. J. Rona, *J. Org. Chem.*, **40**, 2263 (1975).

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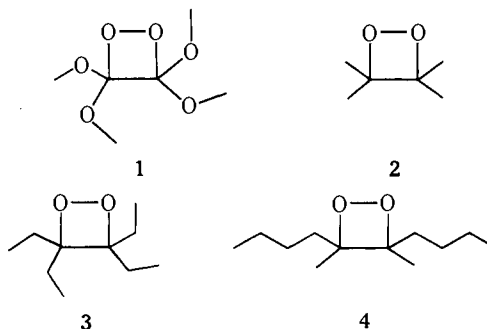
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Received March 4, 1976

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 techniques⁴ 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**.



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.

Table I

Dioxetanes	Rates at 83° (s ⁻¹)	Log A ^a	E _a ^a (kcal/mol)	E _a ^b (kcal/mol)	¹ φ ^c (hν/molecule)	³ φ ^c (hν/molecule)
3	2.2 × 10 ⁻⁴	14.8	30.0 ± 1	31.0 ± 1	0.002 ^d	0.5 ± 0.1
4	1.0 × 10 ⁻³	12.5	25.2 ± 1	26.0 ± 1	0.0008 ^e	0.25 ± 0.05 ^e

^a From Arrhenius plots of chemiluminescence decay rates, in xylenes, with or without various fluorescers: DPA, DBA, perylene, or rubrene. Initial dioxetane concentration range: 10⁻² to 10⁻⁵ M. ^b From temperature drop experiments with DPA or perylene as fluorescer, in xylenes. ^c In xylenes, estimated errors on ¹φ are 50%. ^d 3 concentration = 3.0 × 10⁻⁴ M, temperature 69.0°. ^e 4 concentration = 1.1 × 10⁻³ M, temperature 46.8°.

The activation energies calculated from Arrhenius plots of the rates of chemiluminescence decay are in excellent agreement with the values of E_a obtained by the temperature-drop method in the presence of DPA (Table I). The activation parameters for 4 agree with the literature values.⁶

Both 1 and 3 are more stable than 2, but for different reasons, since in the case of 1 entropy factors seem important whereas energy limitations play the major role in the case of 3. The results with 3 show that simple geometrical considerations alone cannot explain the greater stability of 1 compared to 2. Because of the methoxy groups, the thermolysis of 1 is considerably more exoergic² than that of 2, 3, or 4. On the other hand, the levels of the excited states of methyl carbonate may be appreciably higher than that of the ketones of the other dioxetanes. How these factors and the electronic configuration of the excited carbonyl affect the activation parameters is unclear.

The yields of excited singlet (¹φ) and triplet (³φ) ketones from these two dioxetanes were obtained by the DPA/DBA method, as described earlier⁴ (Table I). Dienes (*cis*-1,3-pentadiene or 2,5-dimethyl-2,4-hexadiene) effectively quench the emission from DBA, while having very little effect on the luminescence enhanced by DPA. Stern-Volmer plots of diene quenching of the chemiluminescence with DBA gave the following values for k_qτ_T: 180 M⁻¹ for 3, 250 M⁻¹ for 4, in xylenes as solvent. These values are consistent with the values of k_{ET}τ_T⁷ obtained from the ratio intercept/slope of the double reciprocal plots of chemiluminescence intensity vs. DBA concentration (k_{ET} and k_q should both be nearly diffusion-controlled). Regarding 4, one point deserves further discussion. The values of k_qτ_T from this work in xylenes are nearly an order of magnitude larger than the triplet quenching slope of 30 M⁻¹ reported by Darling and Foote in decalin.³ In this solvent,⁸ by the chemiluminescence method, k_qτ_T and k_{ET}τ_T are ~50 M⁻¹ and the triplet yield obtained is lower also (³φ = 0.09, still much larger than ¹φ = 0.0006);⁹ the thermolysis rates are unchanged.

The properties of dioxetane 4 resemble closely those of 2. The divergence between the results of Darling and Foote and this work may have one of several origins.¹⁰ It may be tempting to speculate that the luminescence method used here "counts" relaxed triplet ketones, whereas the photolimitation and cyclization reactions could conceivably originate from vibrationally excited triplet 2-hexanone. Therefore those excited triplets which did not chance to undergo type II processes may have been missed in the earlier work. This, however, would not account for the discrepancy in the singlet yield, which is much lower than was reported. Another related possibility is that intersystem-crossing efficiencies and quantum yields of type II processes are different when the excited ketones are generated photochemically or from dioxetane thermolysis. An alternative explanation, difficult to discard at this point, is that the analytical accuracy of product determination was not as high as believed by the previous authors.¹¹ In any case, dioxetanes 3 and 4 undoubtedly conform to the rule favoring triplet

products from "stable" dioxetanes yielding n,π* excited ketones.

Acknowledgments. This work was supported by a grant from the National Science Foundation to Professor J. W. Hastings, to whom we express our appreciation. E.J.H.B. gratefully acknowledges the support of Sao Paulo University and of the Fundacao De Amparo A Pesquisa Do Estado De Sao Paulo (BIOQ/FAPESP Program).

References and Notes

- (1) See, for example, (a) E. H. White, J. D. Miano, C. J. Watkins, and E. J. Breaux, *Angew. Chem., Int. Ed. Engl.*, **13**, 229 (1974); (b) N. J. Turro, P. Lechtken, N. E. Shore, G. Schuster, H.-C. Steinmetzer, and A. Yekta, *Acc. Chem. Res.*, **7**, 97 (1974); T. Wilson, *MTP Int. Rev. Sci., Chem. Kinet., Ser. Two*, 1976, and recent papers listed in ref 2.
- (2) T. Wilson, D. E. Golan, M. S. Harris, and A. L. Baumstark, *J. Am. Chem. Soc.*, **98**, 1086 (1976). Data for 1 E_a = 28.6 kcal/mol, log A = 12.9, ³φ = 0.1, ¹φ = 0.01; for 2 E_a = 27.6 kcal/mol, log A = 14.1, ³φ = 0.3, ¹φ = 0.0015.
- (3) (a) T. R. Darling and C. S. Foote, *J. Am. Chem. Soc.*, **96**, 1625 (1974); (b) C. S. Foote and T. R. Darling, *Pure Appl. Chem.*, **41**, 495 (1975).
- (4) As described in ref 2. The results reported here and in ref 2 are therefore directly comparable. The solutions are not degassed. The efficiency of singlet-singlet transfer from carbonyl to DPA is assumed to be 1.0 and that of triplet-singlet transfer from carbonyl to DBA to be 0.2.
- (5) Dioxetanes 3 and 4 were prepared via the bromohydroperoxide route of K. R. Kopecky, J. E. Filby, C. Mumford, P. A. Lockwood, and J.-Y. Ding, *Can. J. Chem.*, **53**, 1103 (1975), chromatographed at ~5° on neutral silica gel:Na₂EDTA (100:1) and eluted with a gradient of pentane:CH₂Cl₂ (1:1); NMR of 3 in CDCl₃ δ 0.838 (t, 6 H, J = 7.4 Hz), 1.959 and 1.986 (two q, 2 pairs of nonequivalent H, J = 7.2 and 7.7 Hz); and NMR of 4 in CDCl₃ δ 0.0925 (t, 6 H, J = 6.5 Hz), 1.10 to 1.60 (m, 8 H), 1.483 and 1.553 (two s, 2:1, trans and cis, 6 H), 1.773 (t, J = 6.5 Hz). VPC analysis of 3 and 4 shows corresponding ketones; these peaks and the chemiluminescence are suppressed by pretreatment of the dioxetanes with triphenylphosphine, which effects their monodeoxygenation. (P. D. Bartlett, A. L. Baumstark, and M. E. Landis, *J. Am. Chem. Soc.*, **95**, 6486 (1973)). The dioxetane concentrations obtained by NMR or VPC were in reasonable agreement (±10%).
- (6) E_a = 25.5 kcal/mol and log A = 12.5, calculated from reported³ ΔH[‡] = 24.8 ± 0.3 kcal/mol and ΔS[‡] = -3.6 ± 1.0 cal/deg between 50 and 80°.
- (7) k_{ET} is the sum of the rates of all deactivation processes of triplet carbonyl by DBA; see ref 2.
- (8) Decalin was treated overnight with concentrated H₂SO₄, washed, neutralized, dried, and distilled under vacuum. VPC showed only the *cis* and *trans* isomers (1:1).
- (9) This solvent effect is being investigated. Note that k_q and k_{ET} are expected to be lower, since decalin is ~3 times more viscous than xylenes. For a recent discussion of solvent effect on type II processes see, for example, P. Borrell and J. D. Holmes, *J. Photochem.*, **2**, 315 (1973/74).
- (10) In view of the discrepancy on the values of ¹φ and ³φ, these were checked by energy transfer measurements to two other fluorescers: (a) perylene as an interceptor of singlet excited ketones and (b) europium tris(thenoyltrifluoroacetate)-1,10-phenanthroline as interceptor of triplet carbonyls via intermolecular energy transfer, followed by intramolecular transfer to Eu³⁺. The results with these enhancers support very well the yields reported in Table I.
- (11) A total yield of *cis*- and *trans*-1,2-dimethylcyclobutanol of 1.30% instead of the reported 1.14% (= 0.67 *cis* + 0.47 *trans*) would have given ³φ = 0.05 and no singlets. Professor Foote (personal communication) believes that the curvature of their diene quenching plot³ remains an argument in favor of an appreciable yield of singlet ketone. We feel, however, that the problems raised by the high concentrations of diene used (low product yields, long reaction times, and possible "solvent" effects) make it difficult for us to comment usefully on this point.

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Received April 14, 1976