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SPIROADAMANTYL STABILIZATION OF SULFUR-SUBSTITUTED 1,2-DIOXETANES

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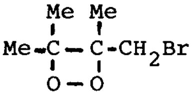
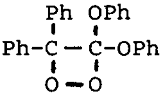
ABSTRACT: With the help of spiroadamantyl substitution, the first sulfur-substituted 1,2-dioxetanes 9 and 10, respectively derived from thiophenylmethyleneadamantane (7) and 2-adamantylidene-1,3-dithian (8) were prepared via singlet oxygenation and detected by NMR.

The stabilizing effect of the spiroadamantyl group on the thermally labile 1,2-dioxetanes is quite convincingly illustrated by the three pairs of dioxetanes 1 - 6. As the $\Delta G^{\neq}_{293.2^{\circ}K}$ values reveal (extrapolated to 293.2°K from reported activation data), the stabilization amounts to ca. 3 - 7 kcal/mol, being most pronounced for the spiroacridanyl derivative 6.



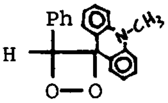
$$\begin{array}{ccc} & Me & Me \\ Me- & C - & C-CH_2Br \\ & O - & O \end{array}$$

(1)



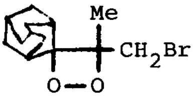
$$\begin{array}{ccc} & Ph & OPh \\ Ph- & C - & C-OPh \\ & O - & O \end{array}$$

(2)



(3)

$\Delta G^{\neq}_{293.2^{\circ}K}$ 26.2[1] 24.1[2] 21.3[2] kcal/mol



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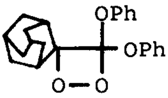

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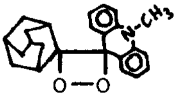
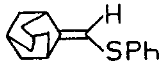


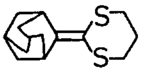
(6)

$\Delta G^{\neq}_{293.2^{\circ}K}$ 29.4[2] 29.2[2] 28.0[3] kcal/mol

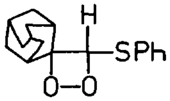
Although the nature of this dramatic stabilizing influence of the spiroadamantal group is as yet not well understood, it should be of synthetic utility for the preparation of hitherto unknown 1,2-dioxetanes. For example, we report here such a successful application in the synthesis of the first sulfur-substituted 1,2-dioxetanes 9 and 10 via photosensitized singlet oxygenation of the thioenol ether 7 [4] and thioacetal 8 [5].



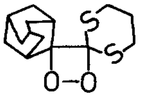
(7)



(8)



(9)



(10)

Thus, a ca. 0.2 M solution of the thioenol ether 7 in $CDCl_3$, containing polymer-bound Rose Bengal as sensitizer, was irradiated with a 150-W sodium street lamp at -70°C under a continuous flow of dry oxygen gas, while monitoring the reaction progress by TLC. After completion of the singlet oxygenation, the suspended Rose Bengal was removed by filtration at ca. -70°C and the filtrate submitted to ^{1}H- and ^{13}C-NMR analysis at -60°C. The characteristic dioxetanyl proton[6] showed up at δ6.16 ppm (singlet) and the carbons at 93.1 ppm (doublet) and 100.2 ppm (singlet). Above -30°C the dioxetane 9 decomposed with light emission quantitatively into adamantanone and thiophenyl formate, as confirmed by IR and NMR. Attempts to purify the dioxetane 9 by low temperature chromatography (-60°C) on Florisil led to complete decomposition, indicating that this dioxetane is still thermally too labile for isolation.

Under similar conditions the dioxetane 10 was prepared from the ketene thioacetal 8, exhibiting the characteristic dioxetanyl carbons[6] at δ96.6 and 109.6 ppm as singlets, respectively for the spiroadamantyl and spiro-1,3-dithianyl carbons. Again, on warm up above -30°C the dioxetane 10 fragmented with weak chemiluminescence into adamantanone and 1,3-dithiane-2-one, as confirmed by IR and NMR. Efforts to isolate dioxetane 10 by low temperature Florisil chromatography led exclusively to the expected fragmentation products.[7]

These preliminary data demonstrate that sulfur-substituted dioxetanes are very unstable, but with the help of spiroadamantyl substitution these "high energy" molecules can be sufficiently stabilized to permit at least spectroscopic detection. The concept of spiroadamantyl substitution should, therefore, prove valuable in the synthesis of other hitherto inaccessible dioxetane derivatives.

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REFERENCES:

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1. W. Adam and K. Sakanishi, Photochem. Photobiol. 30, 45 (1979).
2. L. A. Arias and K. Zinner, unpublished results.
3. F. McCapra, I. Beheshti, A. Burford, R. A. Hann and K. A. Zaklika, J. C. S. Chem. Commun. 1977, 944.
4. F. A. Carey and A. S. Court, J. Org. Chem. 37, 979 (1972).
5. E. J. Corey, D. Seebach and R. Freedman, J. Am. Chem. Soc. 89, 434 (1967).
6. W. Adam, Adv. Heterocycl. Chem. 21, 437 (1977).
7. The fragmentation products are formed essentially quantitatively, indicating negligible attack of $^1O_2$ on sulfur.

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