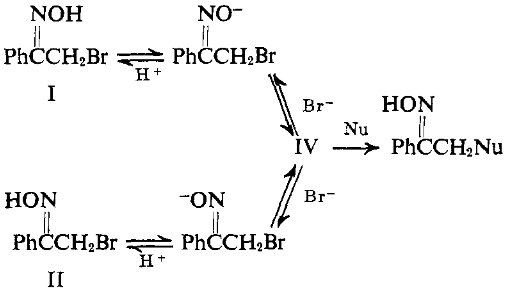
reaction on a preparative scale and performing a $CHCl_3$ extraction, the product responsible for the initial rise in absorbance was identified as *syn*-α-bromoacetophenone oxime (I).

The simplest mechanistic scheme consistent with our observations is illustrated for the α-bromooximes in eq 2 where Nu represents the nucleophilic buffer component. The reactions of both syn and anti isomers proceed through the oxime anions. In the absence of added excess halide ion, the rate-determining step for the solvolysis of both isomers is the loss of halide to form a common intermediate, IV, which we suggest to be α-nitrosostyrene.[13] This intermediate is rapidly trapped by the nucleophile Nu to give a substituted oxime of anti stereochemistry. Apparently, reaction of the intermediate in the s-trans conformation with nucleophiles like morpholine is more rapid than the reaction of the s-cis form,[14] and the anti α-substituted oxime is formed, therefore. In the case of added bromide ion, the intermediate IV is trapped in both the s-cis and s-trans conformations to give both isomers of the α-bromooxime. However, because the *syn*-α-bromooxime I undergoes elimination slower than the anti species II (*vide ante*), the solvolysis of II in the presence of excess Br^- proceeds by way of the initial accumulation of I.



(2)

Attempts to detect directly and positively identify the intermediate IV and related species in the nucleophilic reactions of α-haloalkyl aryl ketooximes in aqueous media are in progress in our laboratory.

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(13) Ample precedent for this hypothesis exists.[3,4,7] α,β-Unsaturated nitroso compounds, for example, have been isolated by the treatment of appropriately sterically hindered α-halooximes with triethylamine in ether. By reaction with piperidine, α-piperidinooximes are produced from these nitroso species (W. Höbold, U. Prietz, and W. Pritzkow, *J. Prakt. Chem.*, **311**, 260 (1969)).

(14) Similarly, *anti*-α-aminoacetophenone oxime esters and ethers undergo the abnormal Beckmann rearrangement about 2×10^3 times faster than the corresponding syn isomers (H. P. Fischer, C. A. Grob, and E. Renk, *Helv. Chim. Acta*, **45**, 2539 (1962)).

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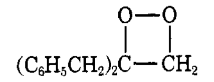
Excited State Carbonyl Species from the Thermal Decomposition of 3,3-Dibenzyl-1,2-dioxetane

Sir:

1,2-Dioxetanes undergo thermal decomposition to produce excited state carbonyl species as evidenced by chemiluminescence[1] and reactions sensitized by the excited state carbonyl species.[1e,2] We now report a type I reaction of an excited state carbonyl moiety produced from the thermal decomposition of a 1,2-dioxetane. Thermal decomposition of $1.04 \times 10^{-3} M$ 3,3-dibenzyl-1,2-dioxetane (**1**) in degassed benzene at 60° produces



$(C_6H_5CH_2)_2C$—CH_2 (O—O ring)

1

bibenzyl and dibenzyl ketone in 2.2 and 88% yield, respectively. Bibenzyl is indicative of triplet dibenzyl ketone, which yields bibenzyl by a type I process.[3] Benzyl chloride is detected in the reaction mixture when **1** is decomposed at 60° in degassed carbon tetrachloride, which indicates that bibenzyl is produced from free benzyl radicals as proposed in the type I process.[3]

Further evidence for excited state carbonyl species from the thermal decomposition of **1** is shown by the production of chemiluminescence when 9,10-diphenylanthracene is incorporated in the reaction mixture. To show that chemiluminescence with 9,10-diphenylanthracene is intimately related to the excited state carbonyl species generated from **1**, quenching of bibenzyl formation with 9,10-diphenylanthracene was measured. An acceptable Stern–Volmer plot (Figure 1) was obtained and from the slope of the plot $k_q\tau$[4] is 20 M^{-1}. Assuming k_q is diffusion controlled (2×10^{10} M^{-1} sec^{-1} in benzene),[5] the lifetime (τ) of triplet dibenzyl ketone is 10^{-9} sec. This is in reasonable agreement with photochemical studies,[3] which indicate that triplet dibenzyl ketone is extremely short-lived. To ensure that stable anomalous quenchers were not present during the decomposition of **1**, which would lower the yield of bibenzyl, the following control experiment was conducted. The amount of bibenzyl produced from **1** in degassed benzene at 60° was determined. Now this reaction mixture, which contained dibenzyl ketone produced from **1**, and an authentic sample of dibenzyl ketone in benzene were irradiated on a merry-go-round[8] in degassed solutions. In both instances, about the same amount of bibenzyl was produced from irradiation.

Previously we have shown that a two-step mechanism, involving biradical intermediates, adequately accounts for the activation parameters of certain 1,2-dioxetanes.[9]

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(1) (a) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969); (b) P. D. Wildes and E. H. White, *J. Amer. Chem. Soc.*, **93**, 6286 (1971); (c) S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970); (d) T. Wilson and A. P. Schaap, *ibid.*, **93**, 4126 (1971); (e) N. J. Turro and P. Lechtken, *ibid.*, **94**, 2886 (1972); (f) J. H. Wieringa, J. Strating, H. Wynberg, and W. Adam, *Tetrahedron Lett.*, 169 (1972); (g) W. Adam and J.-C. Liu, *J. Amer. Chem. Soc.*, **94**, 2894 (1972); W. H. Richardson and V. F. Hodge, *ibid.*, **93**, 3996 (1971).

(2) (a) E. H. White, J. Wiecko, and D. R. Roswell, *ibid.*, **91**, 5194 (1969); (b) E. H. White, J. Wiecko, and C. C. Wei, *ibid.*, **92**, 2167 (1970); (c) H. Güsten and E. F. Ullman, *J. Chem. Soc. D*, 28 (1970).

(3) (a) P. S. Engel, *J. Amer. Chem. Soc.*, **92**, 6074 (1970); (b) W. K. Robbins and R. H. Eastman, *ibid.*, **92**, 6076 (1970).

(4) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 93.

(5) Calculated from the Debye equation[6] with 3.877×10^{-3} P as the viscosity of benzene at 60°.[7]

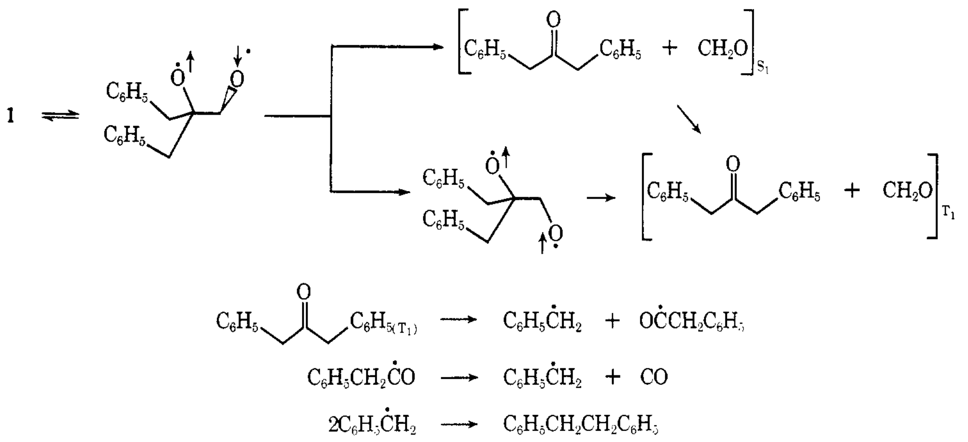
(6) Reference 4, p 95.

(7) "Annual Tables of Constants and Numerical Data Chemical, Physical, and Technological," Vol. 5, Interscience, New York, N. Y., 1971–1972, p 51.

(8) R. S. N. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965).

(9) (a) H. E. O'Neal and W. H. Richardson, *ibid.*, **92**, 6553 (1970); (b) W. H. Richardson, M. B. Yelvington, and H. E. O'Neal, *ibid.*, **94**, 1619 (1972).

Scheme I



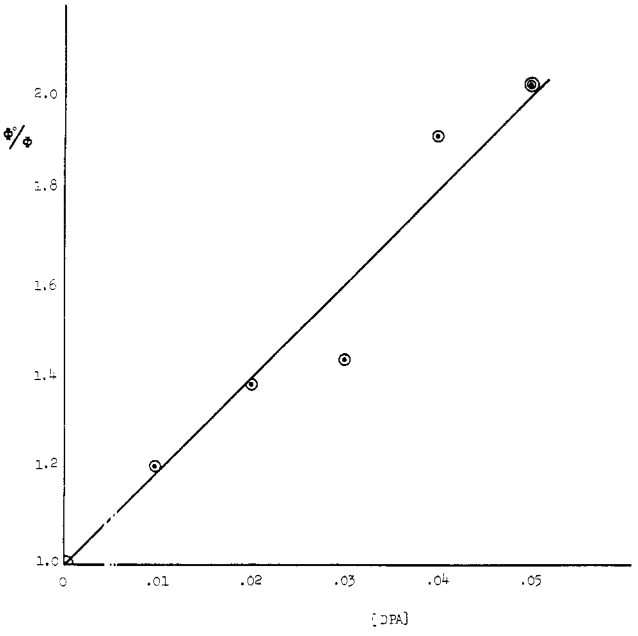


Figure 1. Quenching of bibenzyl production from 1.04×10^{-3} *M* **1** in benzene at 60° with 9,10-diphenylanthracene. In the absence of quencher, $\Phi^0 = 2.2\%$ yield bibenzyl and Φ is the yield of dibenzyl ketone in the presence of 9,10-diphenylanthracene.

An extension of this mechanism which will adequately explain the decomposition of **1** is given in Scheme I. For the two-step mechanism, where the initial step is reversible, a singlet biradical is required. The singlet biradical may undergo spin conversion to the triplet biradical, which can fragment to triplet carbonyl products. Alternately, the singlet biradical may give excited singlet state carbonyl species, which undergo intersystem crossing to the triplet state. This latter route was shown to be relatively unimportant in the thermal decomposition of tetramethyl-1,2-dioxetane.[1e]

Thermochemical calculations indicate that a 1,2-dioxetane can produce only one excited state carbonyl species.[9a] Indeed, recent reports indicate that one excited state carbonyl molecule is produced per 1,2-dioxetane decomposed.[1e,1d] The energy available for the excited state carbonyl species should be partitioned between dibenzyl ketone and formaldehyde as indicated by the brackets. Providing that the excited singlet state pathway is relatively unimportant,[1e,10] the distribution of excited state carbonyl species can be calculated from the triplet state energies of dibenzyl ketone and formaldehyde by the Boltzmann equation. Alternatively, from the yields of bibenzyl and dibenzyl ketone produced from **1** and the photochemical quantum yield for bibenzyl production from triplet dibenzyl ketone ($\Phi = 0.7$),[3] the *difference* between triplet energies of dibenzyl ketone and formaldehyde ($E_{T_{DK}} - E_{T_{CH_2O}}$) is calculated to be 2.2 kcal/mol with the assumption that one excited state carbonyl molecule is produced from **1**.[1e,1d] The triplet state energy of formaldehyde in the gas phase is reported to be 72.5 kcal/mol,[11] while the value for triplet dibenzyl ketone in solution is estimated to be 79 kcal/mol.[3a] The discrepancy between the difference in these reported values (6.5 kcal/mol) and our value of 2.2 kcal/mol may be due to the uncertainty of the reported value for dibenzyl ketone and the fact that the energy for formaldehyde is obtained in the gas phase.

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(10) If the singlet–triplet splittings of the two carbonyl species are similar, the calculated distribution will be valid, even though the S_1 process is important.

(11) J. C. D. Brand and D. G. Williamson, *Advan. Phys. Org. Chem.*, 1, 365 (1963).

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Electron Paramagnetic Resonance of Free Radicals in an Adamantane Matrix. V. Neutral Alkylhydrazyl Radicals

Sir:

We would like to report the first epr detection of neutral alkylhydrazyl free radicals, $R_2N\dot{N}H$, which we have prepared by room temperature X irradiation of the corresponding alkylhydrazines trapped in an adamantane matrix.[1] Although DPPH (α,α-diphenyl-

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(1) D. E. Wood, R. V. Lloyd, and W. A. Lathan, *J. Amer. Chem. Soc.*, **93**, 4145 (1971), and references contained therein.