Communications to the Editor

Biradical Trapping: The Formation of Bicyclic Peroxides via the Thermal and Photodecomposition of Azo Compounds in the Presence of Oxygen

Sir:

The trapping with oxygen of transient species generated photochemically has proven to be a surprisingly useful technique for the preparation of a number of unusual peroxides.[1] Since azo compounds are readily synthesized and provide an excellent source for a wide variety of biradicals, we have investigated the application of oxygen as a biradical trapping agent in azo decompositions.
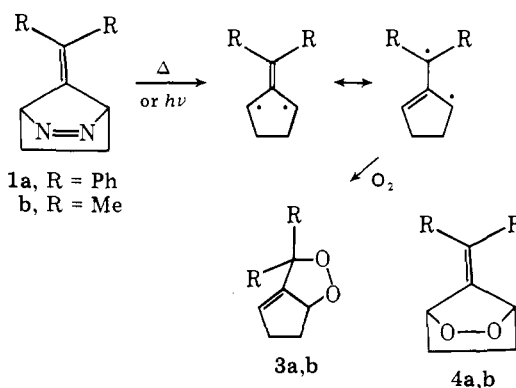
Previous workers have noted the effect of oxygen upon azo decomposition.[2] In both thermally[2b,d,e] and photochemically[2c,f] initiated decompositions, altered product distributions have been observed which imply that oxygen may be trapping the intermediate biradicals. In particular, Berson and co-workers have reported that oxygen chemically quenches the triplet trimethylenemethane biradical.[2d,e] Since trimethylenemethane biradicals are known to have triplet ground states,[3] and to be unusually long-lived species, they seemed to be particularly good candidates for initial oxygen trapping experiments.

Indeed when the azo compounds 1a[3c,4] and 1b[4] either were heated at 40 °C in CCl$_4$ or in CFCl$_3$ solution for 36 to 51 h, or when 1b was irradiated with the ultraviolet lines (351.1 and 363.7 nm) of an argon ion laser for 60 h, in each instance under a medium-pressure (80 to 150 psi) atmosphere of oxygen, the complete suppression of the usual dimeric hydrocarbon products was observed. In their place, peroxides were formed as judged by positive ferrous thiocyanate[5] development of reaction mixture chromatograms. These peroxides could be isolated by column chromatography on silica gel (40% for 3a, Scheme I) followed by microdistillation in the case of 3b (37%, Scheme I). These ring-fused peroxides displayed the usual stability noted previously for substituted 1,2-dioxalanes of this type[6] and had spectral properties in accord with the proposed structures. 3a: mp 77.3–77.9 °C; δ (ppm) (CCl$_4$), –CH$_2$– (2.1, complex, 2 H), allylic –CH$_2$– (2.7, complex, 2 H), >CHO– (5.25, complex, 1 H, decoupled from 2.1 signal), –CH=C< (5.45 doublet of doublets, J = 2 Hz and J' = 3 Hz, 1 H), C$_6$H$_5$ (7.1, complex, 10 H); m/e 264. 3b: liquid; δ (ppm) (CFCl$_3$), two CH$_3$'s (1.30 and 1.40 singlets, 3 H each), –CH$_2$– (1.4–2.3, complex, 2 H), allylic –CH$_2$– (2.75, multiplet, 2 H), >CHO– (5.25, complex, 1 H), –CH=C< (5.45, doublet of doublets, J = 3 Hz and J' = 2 Hz, 1 H); m/e 140. Under none of the aforementioned conditions was the formation of the bridged peroxides 4a,b established, although this could well be due to the expected lability of this more strained system.
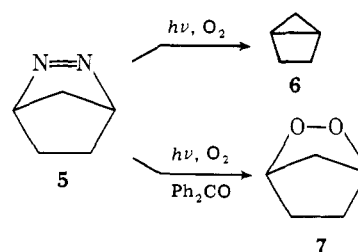
Even though the formation of peroxides 3a,b demonstrates the feasibility of the oxygen trapping of biradicals generated from azo compounds, these experiments do not provide a rigorous test of this method since the trimethylenemethane biradicals are so readily trappable owing to the existence of an accessible and long-lived triplet ground state. In order to evaluate this technique with shorter lived biradical species, we also have examined the decomposition of azo compound 5[7] in the presence of oxygen. The biradical derived from 5 has been studied thoroughly[8] and is known to have a short-lived triplet ground state.[9]

Trapping experiments under thermal conditions are not feasible in the case of 5 since temperatures in the range of 180

Scheme I

1a, R = Ph
b, R = Me

3a,b

4a,b

Scheme II

5

6

7

°C would be required.[7] Direct irradiation of 5 produces the singlet biradical which collapses to bicyclo[2.1.0]pentane (6) before it can be trapped by oxygen (150 psi). However, the benzophenone-sensitized photodecomposition of 5 directly produces the triplet biradical which is trapped to afford peroxide 7 (Scheme II). In order to obtain reproducible and optimum yields in this reaction, careful attention must be devoted to experimental conditions. Since direct excitation of 5 leads to very efficient formation of 6, it is essential to irradiate *only* the benzophenone chromophore. This is done by using an excess of benzophenone (0.6 M benzophenone: 0.3 M 5), and irradiating either with the ultraviolet lines of an argon ion laser or with a 1000-W xenon–mercury lamp with careful filtration of the output to remove all wavelengths of light shorter than about 350 nm.[10] It will be recognized that the benzophenone triplets may be quenched by either oxygen, the azo compound 5, or the peroxide 7. Thus, optimum oxygen pressures seem to be about 150 psi. At oxygen pressures higher than about 225 psi, oxygen quenching dominates to the extent that no reaction occurs.[11] Sensitized decomposition of the peroxide 7 becomes increasingly important as the reaction proceeds: irradiation time, % azo conversion, % yield peroxide: 16 h, 21%, 73%; 64 h, 54%, 43%. The peroxide 7 was usually isolated after about 60 to 70 h of irradiation in CFCl$_3$. Removal of the CFCl$_3$ at –78 °C, microdistillation of the volatile components in the residue, and column chromatography of the distillate on silica gel (CHCl$_3$–CFCl$_3$)[12] afforded pure 7. This material had spectral properties identical with those of an authentic sample,[13] and upon catalytic hydrogenation (Pd/C) yielded *cis*-1,3-cyclopentanediol which gave a bis(phenylurethane) derivative that was identical with an authentic sample.[14]

The examples outlined above would seem to demonstrate that oxygen trapping of azo-derived triplet biradicals provides a new and versatile technique for the preparation of peroxides.

In particular, the synthesis of peroxide **7** establishes this method along with the elegant procedures of the Salomons[15a] and Porter[15b] as a potential method for the synthesis of prostaglandin endoperoxides.

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References and Notes

(1) R. M. Wilson, E. J. Gardner, R. C. Elder, R. H. Squire, and L. R. Florian, *J. Am. Chem. Soc.*, **96**, 2955 (1974); R. M. Wilson and S. W. Wunderly, *Chem. Commun.*, 461 (1974); R. M. Wilson and S. W. Wunderly, *J. Am. Chem. Soc.*, **96**, 7350 (1974); R. M. Wilson, S. W. Wunderly, J. G. Kalmbacher, and W. Brabender, *Ann. N.Y. Acad. Sci.*, **267**, 201 (1976); R. M. Wilson, R. Outcalt, and H. H. Jaffé, *J. Am. Chem. Soc.*, in press; oxygen trapping of 1,4-biradicals derived from aryl ketone addition to olefins has also been observed: R. M. Wilson and Fiona Geiser, unpublished results.
(2) (a) N. J. Turro, C. A. Renner, W. H. Waddell, and T. J. Katz, *J. Am. Chem. Soc.*, **98**, 4320 (1976); (b) Y. C. Toong, W. T. Borden, and A. Gold, *Tetrahedron Lett.*, 1549 (1975); (c) W. D. K. Clark and C. Steel, *J. Am. Chem. Soc.*, **93**, 6347 (1971); (d) J. A. Berson, C. D. Duncan, and L. R. Corwin, *ibid.*, **96**, 6175 (1974); (e) J. A. Berson, L. R. Corwin, and J. H. Davis, *ibid.*, **96**, 6177 (1974); (f) R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966); (g) P. S. Engel, *ibid.*, **91**, 6903 (1969); (h) J. A. Kerr, "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, pp 3, 29.
(3) (a) R. J. Baseman, D. W. Pratt, M. Chow, and P. Dowd, *J. Am. Chem. Soc.*, **98**, 5727 (1976); (b) B. K. Carpenter, R. D. Little, and J. A. Berson, *ibid.*, **98**, 5723 (1976); (c) M. S. Platz, J. M. McBride, R. D. Little, J. J. Harrison, A. Shaw, S. E. Potter, and J. A. Berson, *ibid.*, **98**, 5725 (1976).
(4) J. A. Berson, R. J. Bushby, J. M. McBride, and H. Tremelling, *J. Am. Chem. Soc.*, **93**, 1544 (1971). These azo compounds were prepared using a modified procedure going through the copper complexes of the azo compounds: P. G. Gassman and K. T. Mansfield, *Org. Syn.*, **5**, 96 (1967).
(5) R. A. Johnson and E. G. Nidy, *J. Org. Chem.*, **40**, 1680 (1975).
(6) W. Adam and J. Arce, *J. Am. Chem. Soc.*, **97**, 926 (1975).
(7) Azo compound **5** was synthesized by the method of Gassman.[4]
(8) Clark and Steel[2c] have observed the suppression of the hydrocarbon products in the photochemical decomposition of **5**, and speculated that this was due to the oxygen trapping of the biradical. However, they did not report the isolation of any products arising from this trapping.
(9) S. L. Buchwalter and G. L. Closs, *J. Am. Chem. Soc.*, **97**, 3857 (1975).
(10) The following filter system is used at present: (a) Oriel glass filter (G774-3550); (b) Oriel infrared-absorbing glass filter (G776-7100); (c) 10-cm cell of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate (0.02 g/10 mL of H₂O); 1-cm cell of *p*-methoxyacetophenone (0.01 g/10 mL of benzene).
(11) We thank N. J. Turro and W. Cherry for informing us of this upper limit of the oxygen pressure.
(12) The chromatography operation is necessary to remove unreacted azo compound **5** and small amounts of peroxide **7** decomposition products, principally, cyclopentenone and levulinaldehyde.
(13) The proton NMR and IR spectra of peroxide **7** were kindly provided by N. A. Porter.
(14) C. Kaneko, A. Sugimoto, and S. Tanaka, *Synthesis*, **12**, 876 (1974); L. N. Owens and P. N. Smith, *J. Chem. Soc.*, 4035 (1952).
(15) (a) R. G. Salomon and M. F. Salomon, *J. Am. Chem. Soc.*, **99**, 3501 (1977); (b) N. A. Porter and D. W. Gilmore, *ibid.*, **99**, 3503 (1977).
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*Department of Chemistry, University of Cincinnati*
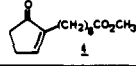*Cincinnati, Ohio 45221*
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Lanthanides in Organic Chemistry. 1. Selective 1,2 Reductions of Conjugated Ketones[1]

Sir:

Although rare earth complexes have enjoyed considerable utility as shift reagents in NMR spectroscopy,[2] there are limited applications of these elements in synthetic chemistry. With the exception of cerium[4+], which is employed as an efficient oxidation agent,[3] the lanthanides have received only limited uses as catalysts, in petrochemical reactions,[4] epoxide rearrangement,[5] or optical resolution,[6] and an unusual reaction of secondary amines with acetonitrile.[7] Recent reports[8] con-

Table I

Starting material[a]	Lanthanides used	Yields[b]	Allylic alcohol[c]	Saturated alcohol[d]
1	none*	100*	89	11
	Ce	100	100	0
2	none	100	0	100
	Ce	100	97	3
	Sm	100	94	6
	Eu	100*	93	7
3	none	95*	38	62
	Sm	96*	96	4
	Ce	100	99	1
4 (CH₂)ₙCO₂CH₃	none	100	95	5
	Sm	92	100	0
5	none	100*	51	49
	Sm	98	93	7
	Ce	100	>99	traces
6	none	98*	90	10
	Ce	100	100	0
7	none	98*	90	10
	Ce	100	100	0

[a] The following standard procedure was adopted: 1 mmol of starting material is dissolved in 2.5 mL of the 0.4 M LnCl₃·*n*H₂O methanol solution and NaBH₄ (1 mmol) is slowly added (2 min) with stirring. The mixture is allowed to react for 3–5 min, followed by hydrolysis and extraction with ether. [b] Isolated yields except in specified cases (asterisk) in which they were obtained by VPC (2 m × 2 mm i.d. Carbowax 20M column on Chromosorb WAW, 15 mL of N₂/min Carlo Erba Fractovap 1501 chromatograph). [c] Identification of these compounds was made by the usual spectral methods (IR, UV, NMR) and by comparison with authentic samples. [d] The relative percentage of these reduction compounds and their identity were ascertained by TLC and/or VPC.

cerning the synthetic potential of lanthanides prompt us to communicate our preliminary results using rare earth halides and sodium borohydride for the selective conversion of α,β-unsaturated ketones to allylic alcohols.

Treatment of an equimolecular amount of a ketone (2-hexanone, cyclohexanone, acetophenone) and samarium chloride hexahydrate in ethanol[9] with sodium borohydride (1 molar equiv) produces an evolution of hydrogen coupled with a quantitative yield of the corresponding alcohol in 5–10 min. Application of this procedure (in methanol[9]) to α,β-unsaturated ketones produced high yields of the corresponding allylic alcohols, in many cases uncontaminated with the 1,4 reduction product. Several representative examples are presented in Table I.

Such selectivity has been noted with other reducing systems,[10] but the previous methods usually suffer from limitations. Thus, of the recently developed reagents, NaBH₃CN,[11] is unreliable with certain cyclic enones, giving mixtures resulting from 1,2 and 1,4 additions. 9-Borabicyclononane (9-BBN) has a decreased reactivity with sterically hindered carbonyl groups,[12] which requires long reaction times and/or refluxing solvent for reduction. Diisobutylaluminium hydride (Dibah) is not selective for carbonyl groups[13] and must be used at low temperature. The last two reagents are expensive and require anhydrous conditions in an inert atmosphere.

Of the lanthanides tested, samarium and cerium appear to offer the best combination of yield and selectivity (Table I). The method evidently offers the following advantages. First, nearly exclusive selective 1,2 reduction is obtained under conditions which do not affect carboxylic acids, esters, amides, halides, and cyano and nitro groups.[14] Even 2-cyclopentenone, which is especially prone to undergo the 1,4 addition reaction, can be reduced to 2-cyclopentenol with a selectivity as high as 97%. Furthermore, the reactions may be conducted at room temperature, without special exclusion of air or moisture, and