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Photorearrangement of α-Azoxy Ketones and Triplet Sensitization of Azoxy Compounds

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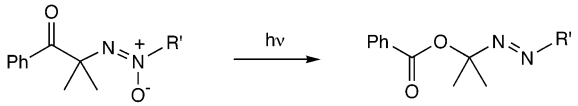


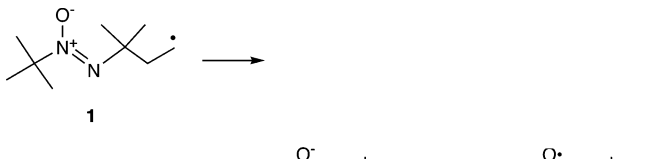
4 a R' = t-Bu b R' = Ph **8**

Although some aspects of azoxy group radical chemistry have been investigated,[1] unhindered α-azoxy radicals remain poorly understood. Here we report the generation of α-azoxy radicals under mild conditions by irradiation of α-azoxy ketones **4a**,**b**. These compounds undergo α-cleavage to yield radicals **5a**,**b**, whose oxygen atom then recombines with benzoyl radicals to produce presumed intermediate **15**. Formal Claisen rearrangement gives α-benzoyloxyazo compounds **8a**,**b**, which are themselves photolabile, leading to both radical and ionic decomposition. The ESR spectrum of **5a** was simulated to extract the isotropic hyperfine splitting constants, which showed its resonance stabilization energy to be exceptionally large. Azoxy compounds have been found for the first time to be good quenchers of triplet excited acetophenone, the main sensitized photoreaction of **7*Z*** in benzene being deoxygenation. While this reaction has been reported previously, it was always in hydrogen atom donating solvents, where chemical sensitization occurred. The principal direct irradiation product of **4b*Z*** and model azoxyalkane **7*Z*** is the *E* isomer, whose thermal reversion to *Z* is much faster than that of previously studied analogues.

Introduction

Despite its occurrence in a number of biologically active molecules,[2−7] the azoxy functional group has received less attention than its lower oxidation state analogue, the aliphatic azo group.[8] The latter is a widely used source of free radicals, but as pointed out in a recent review,[1] the radical chemistry of azoxy compounds is relatively sparse.

Several years ago, we reported that γ-azoxy radical **1** generated from a perester precursor undergoes fragmentation to ethylene with a rate constant below 2×10^5 s^{-1} at 120 °C.[9] Mysteriously, we were unable to find any



1 **2** **3**

product attributable to the expected α-azoxy radical **2**, also named hydrazonyl oxide **3**. On the other hand,

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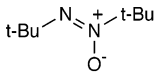
TABLE 1. UV Extinction Coefficients of Azoxy and Azo Compounds



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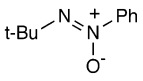


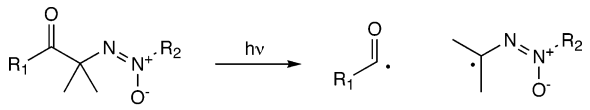
7Z

compd	ϵ (313 nm)	ϵ (366 nm)
4a	128	16
4b*Z*	830	22
8a	4.7	26
8b	212	80
6	32	1.9
7*Z*	262	7.7
PhCOMe	41	6.7

bromination of azoxy compounds is known to occur at the distal carbon, presumably via α-azoxy radicals.[3,10]

Results

The goal of the present work was to generate α-azoxy radicals under mild conditions in hopes of learning more about their chemistry. Having failed to synthesize azo or perester precursors to **2**, we turned to the Norrish Type I photochemical cleavage of α-azoxy ketone **4**, a previ-



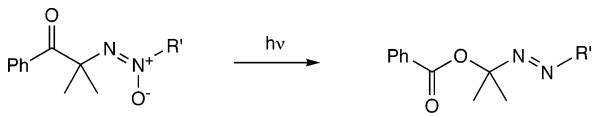
4 **5**

a: R_1 = Ph, R_2 = t-Bu
b: R_1 = Ph, R_2 = Ph
c: R_1 = $PhCH_2$, R_2 = t-Bu

ously unknown structural type. Photolysis of some phenones and benzyl ketones yields alkyl radicals in solution;[11−17] hence, it is not unreasonable that **4a**−**c** might also exhibit α-cleavage.

Photochemistry of 4a. The extinction coefficients of **4a** at two photochemically useful wavelengths are included in Table 1, and the spectra can be found in the Supporting Information. The bichromophoric molecule absorbs twice as strongly as the sum of its two individual chromophores, represented by acetophenone and azoxy-*tert*-butane **6**.[18] Irradiation of **4a** in benzene at 313 nm and 25 °C caused clean rearrangement to an unexpected product, azoester **8a**, whose UV data are included in Table 1. The quantum yield for appearance of **8a** was 0.02 at 23, 60, and 100 °C, and the reaction even proceeded at −78 °C.

The disappearance rate of **4a** was not diminished by the inclusion of 0.1 M biphenyl[19] as quencher, but 0.1 M 1,3-cyclohexadiene, a quencher of much lower triplet

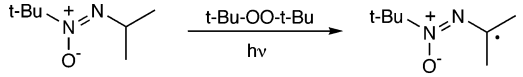


4 **8**

a R' = t-Bu
b R' = Ph

energy than biphenyl, decreased the conversion of **4a** to **8a** by 18.1%, corresponding to a Stern−Volmer $k_q\tau$ of 1.77. To determine whether α-cleavage of the ketone moiety was on the pathway from **4a** to **8a**, we trapped[20,21] the benzoyl radicals with *tert*-butyl thiol. Irradiation of **4a** at 313 nm with 0.16 M *tert*-butyl thiol afforded benzaldehyde in 25% yield, as determined by NMR. A corresponding reduction in the amount of **8a** was observed but no product from trapping of **5a** could be identified.

The photolysis of **4a** was also investigated by ESR spectroscopy. Irradiation of **4a** in toluene-d_8 at +8 °C with a full 500 W mercury arc lamp gave a weak but structured ESR signal. Suspecting that the signal was due to radical **5a**, we generated this intermediate independently by irradiation of di-*tert*-butyl peroxide[22,23] containing *tert*-butyl(ONN)azoxy-2-propane **9** at −78 °C. A stronger signal ∼60 G wide containing about 37 lines was observed and was very similar in appearance to the one from **4a** (cf. Supporting Information). The GC trace



9 **5a**

of the irradiated solution showed several peaks, none of which were in the right region for the C−C dimer of **5a**.[9] To support the assignment of the ESR signals to **5a**, the experiment with **9** was repeated at −50 °C using better ESR equipment. The superior resolution (cf. Supporting Information) allowed isotropic simulation (correlation coefficient 0.926) with the program WinSim,[24] which led to the following splitting constants: N1 13.75 G, N2 1.91 G, 3H 5.64 G, 3H 5.12 G. A second radical was present in the spectrum but since its intensity was much lower than that of **5a**, this minor species was not studied further.

Photochemistry of 4b*Z*. As shown in Table 1, **4b*Z*** absorbs about three times more strongly at 313 nm than the sum of its two chromophores, which are represented by acetophenone and **7*Z***.[25−27] Irradiation of **4b*Z*** at 313 nm both at 25 and −78 °C gave the intensely yellow **8b**, but the major reaction was *Z* → *E* photoisomerization

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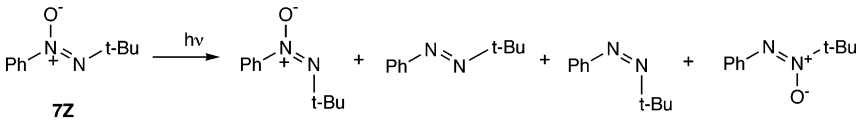
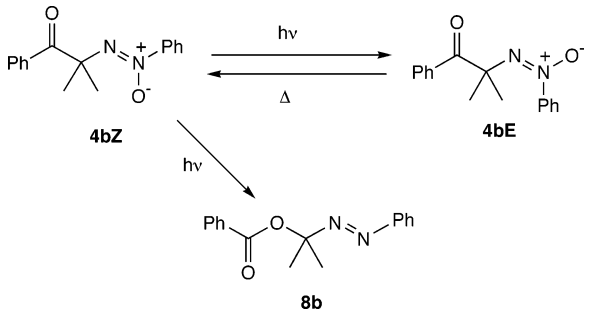
TABLE 2. Relative GC Peak Areas in the Direct and Sensitized Photolysis of 7Z at 366 nm in Toulene-d_8



	7E	10E	10Z	11
direct photolysis[a]	27%	3%	1%	4%
triplet sensitized[b]	10%	25%	7%	1%

[a] Conditions: −5 °C, 4 h, 62% of **7Z** left unreacted. [b] Conditions: PhCOMe, −5 °C, 4 h, 58% of **7Z** left unreacted.

SCHEME 1. Photoreactions of 4b*Z*



about the azoxy double bond.[28−30] The E isomer (**4bE**) reverted to the *Z* isomer **4b*Z*** with a half-life of 14 min at 50 °C. This behavior supports the structural assignment of **4b*E*** but additionally, the chemical shift changes in toluene-d_8 upon *Z*−*E* isomerization (**4b*Z*** Me_2 1.716 ppm vs **4b*E*** Me_2 at 1.377 ppm) are similar to those of **7*Z*** → **7*E*** (1.472 vs 0.943 ppm). The magnitude of the upfield shift upon *Z* → *E* isomerization is larger than that in the methyl and ethyl analogues.[29] Irradiation of **4b*Z*** at ambient temperature and 313 nm in acetone-d_6 as solvent and triplet sensitizer[31−34] exhibited the same rearrangement quantum yield as in toluene-d_8. Irradiationof **4b*Z*** in toluene at −53 °C in the ESR cavity led to a weak signal about 50 G wide consisting of 13 peaks, which were much broader than those from **4a**. This spectrum was definitely not due to phenyldiazenyl radicals[35] arising from secondary photolysis of **8b**. Instead, the similarity of the major nitrogen coupling to that of **5a** suggests that this radical is **5b**.

Irradiation of 4c. This compound was designed to decarbonylate photochemically but it proved to be quite photostable. Thus **4c** upon irradiation with an unfiltered 500 W mercury lamp gave neither **8c** nor the *E* azoxy isomer but instead slowly decomposed to a mixture of many products.

Triplet Sensitization of Model Azoxy Compounds. Because the photorearrangement of **4b*Z*** in acetone-d_6 is the first reported triplet sensitized reaction of an azoxy compound, we examined the azoxy group as a triplet quencher. Acetophenone was chosen as the donor because of its high triplet energy (73.6 kcal/mol),[36] its structural similarity to the ketone moiety of **4**, and because it is known to phosphoresce in solution.[37] Azoxy-*tert*-butane **6** (0.012 M) and phenylazoxy-*tert*-butane **7*Z*** (0.0021 M) were found to be strong quenchers of acetophenone emission intensity. The quenching rate constant in isooctane was obtained by quenching the triplet lifetime of acetophenone, giving k_q values of 9.8×10^8 M^{-1} s^{-1} for **6** and 4.4×10^9 M^{-1} s^{-1} for **7*Z***.

Since **6** and **7*Z*** proved to be good triplet quenchers, we decided to investigate the triplet sensitized photochemistry of **7*Z***. Two degassed and sealed NMR tubes were prepared, one containing 0.0191 M **7*Z*** in toluene-d_8 and the other containing the same concentration of **7*Z*** plus 0.437 M acetophenone. The high concentration of acetophenone was needed to make it the main light absorber because the extinction coefficient of **7*Z*** exceeded that of acetophenone at 366 nm (cf. Table 1). Irradiating both tubes in parallel for 4 h at 366 nm led to the same products but in different amounts (cf. Table 2). Whereas *Z* → *E* isomerization was dominant under direct irradiation, this process is actually negligible with acetophenone present. We calculate that 4.6% of the incident light was absorbed directly by **7*Z*** in the sensitized experiment, as compared to 16% in the direct irradiation, where the overall absorbance was only 0.073. Since the contribution of direct photolysis in the sensitized reaction was 4.6/16 = 29%, the bulk of the **7*E*** seen in the latter case arose by direct irradiation of **7*Z***.

The photoisomer **7*E*** was thermally labile, exhibiting a half-life for reversion to **7*Z*** of 2.3 h at 25 °C. Due to steric repulsion, **7*E*** is much more labile than its ethyl analogue, which reverts completely to the *Z* isomer in 5 h at 110 °C.[29] On the other hand, **7*E*** is slightly more stable than **10*Z***, whose half-life for conversion of **10*E*** is 1.36 h at 25 °C.[38] The set **7*E***, **10*Z*** provides a rare opportunity to compare the thermal isomerization rate of a cis azoalkane with that of its related azoxy compound.

Deoxygenation was the main process observed under triplet sensitization but the fate of oxygen is unknown. The structure of the deoxygenated product, phenylazo-

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TABLE 3. ^{15}N Chemical Shifts[a]

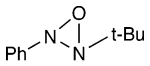
	7Z calc	**7Z** obs	**7E** calc	**7E** obs	**12** calc
N[b]	1.2	−20.2	30.8	1.4	−115.4
N[c]	−39.7	−52.1	−23.9	−42.0	−164.3

[a] ppm from nitromethane standard. [b] Nitrogen proximal to the *tert*-butyl group. [c] N−O.

tert-butane **10*Z*,*E***, was proven by comparison with an authentic sample.[39,40] The sensitized irradiation was repeated in C_6D_6 to rule out hydrogen abstraction from the solvent, but the outcome was the same.

Because direct irradiation of azoxy compounds can led to oxadiaziridines[28,41−43] as well as $Z \rightarrow E$ isomerization,[28−30] it was important to verify the structure of **7*E*.** Surprisingly,[44] no ^{1}H NOE was seen for the *tert*-butyl protons and the ortho H's of the aromatic ring. This negative result prompted us to examine the NOE of a model compound **10*Z***, whose trans−cis photoisomerization is well-known.[38] Since **10*Z*** also failed to exhibit NOE, we resorted to comparing experimental ^{15}N chemical shifts with those calculated theoretically,[45] as shown in Table 3. The proximal and distal nitrogens were assigned unambiguously by ^{1}H−^{15}N HMBC.

Although the calculated shifts are 10−20 ppm downfield from the observed value for **7*Z***, the predicted direction and magnitude of the changes upon $Z \rightarrow E$ isomerization lie within 8 ppm of the observed value. The chemical shifts of oxadiaziridine **12** are calculated to fall drastically upfield from those of **7*Z*,*E***, ruling out **12** as the photoisomer.



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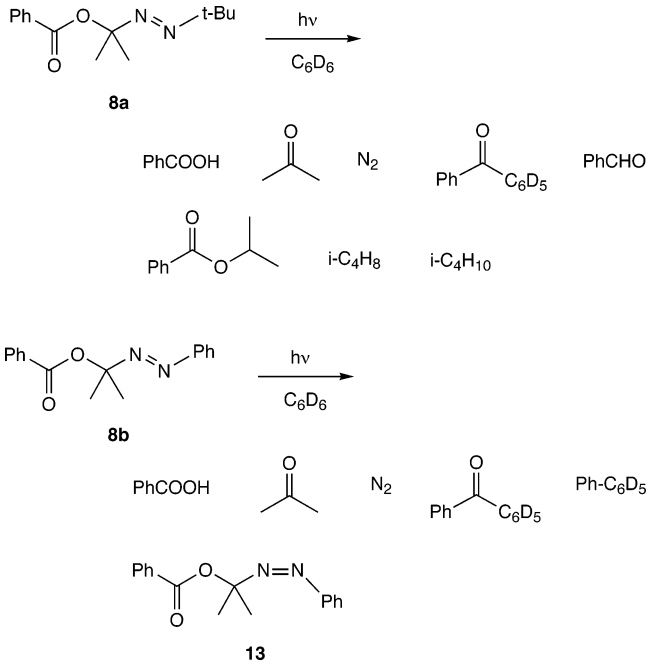
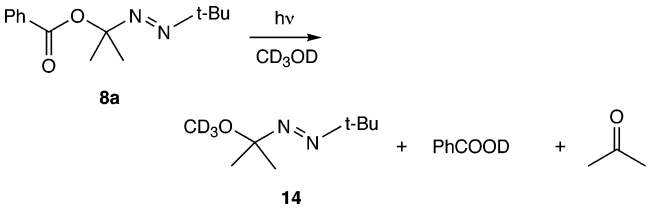
Additional support for the structure of **7E** was provided by its independent synthesis from **10*Z***. A solution of **10*E*** in toluene-d_8 was irradiated in an NMR tube with a 150 W xenon lamp until the **10*Z***:**10*E*** ratio was 0.35. The mixture was oxidized in situ with MCPBA, resulting in the clean conversion of all **10*Z*** to **7*E*** within 10 min. The *tert*-butyl group of **7*E*** ($\delta = 0.943$ ppm) exhibited a sizable upfield shift in toluene-d_8 relative to that of **7*Z*** (1.472 ppm), just as in the azo precursors (**10*E*** 1.311; **10*Z*** 1.090).[29] After **10*Z*** had disappeared, the oxidation of **10*E*** continued at a much slower rate and oxygen was introduced proximal[18] to the *tert*-butyl group to yield major product **11** accompanied by ∼6% **7*Z***. The reversal of oxidation regiochemistry between **10*E*** and **10*Z*** is noteworthy and apparently unprecedented since the only acyclic cis azoalkane oxidized previously was symmetrical.[28]

Secondary Photolysis of Azoesters. As seen in Table 1, the azoester products **8a**,**b** absorb enough light to undergo secondary photoreactions and in fact these can complicate the mechanistic interpretation of azoxy ketone photolysis. Irradiation of authentic **8a**,**b** yielded nitrogen plus a mixture of products, as shown below. In **8b** only, decomposition was accompanied by isomerization to the cis azo isomer **13**. Because it was initially



surprising to find benzoic acid as the major product of **8a**,**b**, the irradiation of **8a** was repeated in MeOH-d_4. We found that the benzoyloxy group was replaced in part by CD_3O to yield **14**, consistent with ionic dissociation of the substituent α to the azo group.[46,47]



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Discussion

Mechanism of 4 to 8. The simplest mechanism for the photorearrangement begins with α-cleavage to benzoyl radical plus α-azoxy radical **5a**. These radicals

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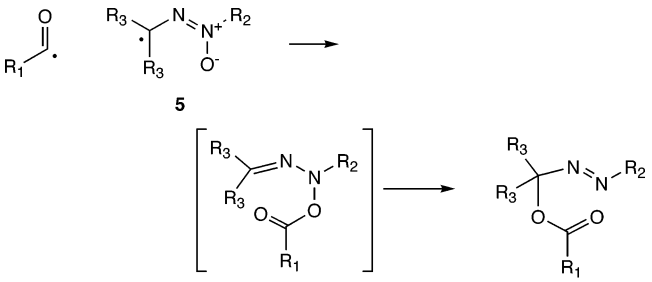
TABLE 4. Calculated Activation Energy for Claisen Rearrangement of 15 to 8

R^1	R^2	R^3	HF, hartrees	TS, hartrees	$\Delta H^{\ddagger}$, kcal/mol
H	H	H	−338.465 327 5	−338.419 204 8	28.9
H_2C=CH−	H	H	−415.868 578 8	−415.828 300 7	25.3
Ph	H	H	−569.530 707 4	−569.490 234 4	25.4
H	H	Me	−417.103 647 5	−417.069 106 5	21.7
H	Me	Me	−456.418 324 7	−456.387 535 6	19.3
H_2C=CH−	Me	Me	−533.822 631 1	−533.789 195 6	21.0

recombine at azoxy oxygen to afford intermediate **15**, which then rearranges to the final product **8**. However,



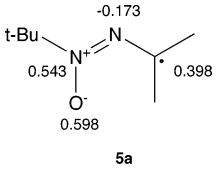
careful scrutiny of the reaction by low-temperature NMR failed to reveal the presence of **15**. We were misled initially by the appearance of broad ^{1}H NMR peaks from **4a** (but not from **4bZ**) that built up to a 1:5 ratio relative to starting material (cf. Supporting Information). Since these peaks reverted to those of **4a** on warming to −25 °C, fell at unreasonable chemical shifts for **15**, and were too labile to be the *E* azoxy isomer, their nature remains obscure.

A literature search revealed no published structures quite like **15**[48−51] and an attempt to generate **15** from acetone *tert*-butyl hydrazone and benzoyl peroxide[52] at 0 °C led cleanly to **8a** and unknown NMR peaks not consistent with **15a**. In hopes of understanding why we failed to observe this postulated intermediate by NMR, the activation energy for Claisen rearrangement was calculated theoretically at the B3LYP/6-31G* level.[45] Table 4 shows that the activation enthalpy lies in the same range as that for the Cope rearrangement.[53] Radical delocalizing substituents R^1 and methyl groups R^2 and R^3 decrease $\Delta H^{\ddagger}$ but not enough to explain our inability to detect **15**. Homolytic dissociation of **15** was calculated to require more energy than the figures in Table 4. Perhaps **15** absorbs UV light as does a peroxide or *N*-chloroamine and **15** → **8** occurs photochemically.

Lacking experimental evidence for **15**, we sought to verify that α-cleavage of **4a** really is the first step of the reaction. Irradiation of this azoxy ketone with *tert*-butyl thiol led to benzaldehyde[20,21] but it was not clear initially whether it came from **4a** or from secondary photolysis of **8a**. However, a plot of benzaldehyde versus time showed a sizable initial slope while a similar plot of acetone, a decomposition product of **8**, showed an initial slope of zero. If benzaldehyde arose solely from secondary photolysis of **8a**, both plots would have exhibited an initial slope of zero. The ESR experiment with **4a** also supports initial α-cleavage since essentially the same spectrum was observed from **4a** and from irradiation of **9** with di-*tert*-butyl peroxide. The nitrogen splitting constants extracted from the latter spectrum (13.75, 1.91 G) are in accord with those of known heavily substituted hydrazonyl oxide radicals (e.g. for t-Bu2C=N^2−N^1($O^{\bullet}$)−Ph, $a(N^1)$ = 12.1 G, a(N^2) = 2.7 G[54] and for t-BuPhC=N^2−N^1($O^{\bullet}$)−t-Bu, $a(N^1)$ = 12.5 G, $a(N^2)$ = 1.7 G[55] and in acceptable agreement with the splittings calculated quantum mechanically[45] (cf. Supporting Information). The proton splittings of **5a** are exceptionally small, reflecting the high degree of radical stabilization that one might expect for this nitroxyl structure.[56] Thus 1,1-dimethylallyl radical exhibits $a(CH_3)$ = 12.22, 15.35 G while **5a** exhibits $a(CH_3)$ = 5.12, 5.64 G. Application of Ruchardt's eq 4,[23] which relates β hyperfine splittings to radical stability, reveals that the resonance stabilization energy of **5a** is 28.1 kcal/mol, which is twice that of the 1,1-dimethylallyl radical.

There remains the possibility that α-cleavage is a side reaction not on the path from **4a** to **8a**. However, in a t-BuSH trapping experiment where 60% of **4a** reacted, the yield of PhCHO was 25% while that of **8a** and its photolysis products was 21% and 15%, respectively. It follows that t-BuSH diminishes the amount of **8a** by an amount very nearly equal to the yield of PhCHO, thus placing PhCO$^{\bullet}$ on the reaction pathway. Since t-BuSH failed to trap **5a**, our only evidence for this radical comes from the ESR experiment.

The low quantum yield for photorearrangement of **4a**,**b** may be attributed to efficient recombination of benzoyl radicals at the original site of attachment. However, the spin density of **5a** is higher at oxygen than at carbon, as



shown by the calculated spin densities below. Moreover, cage recombination of other "allylic" radicals occurs at both ends.[57] Another explanation for the low quantum yield is radiationless decay of excited **4a**,**b**, which could be accompanied by *Z* → *E* isomerization of the azoxy group. To explore the importance of these factors, we undertook a brief investigation of the azoxy group as a triplet energy acceptor.

Triplet Energy Transfer to Model Azoxy Compounds. We report for the first time that azoxyalkanes

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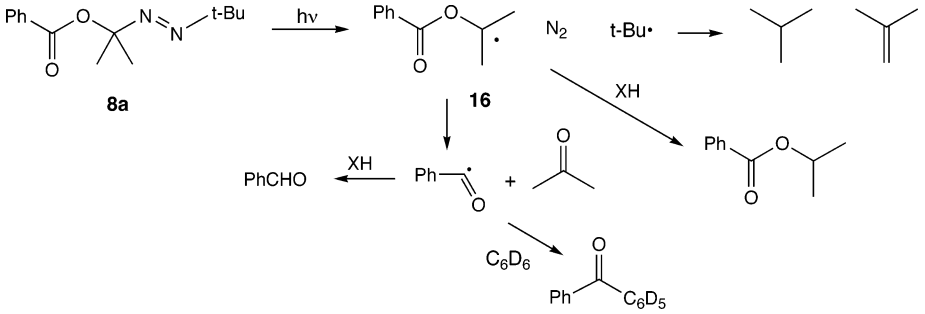
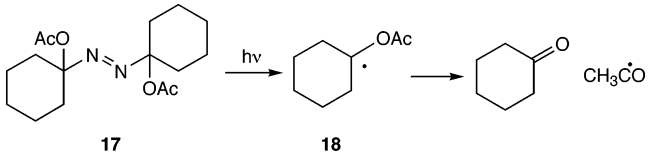
SCHEME 2. Photolysis of 8a



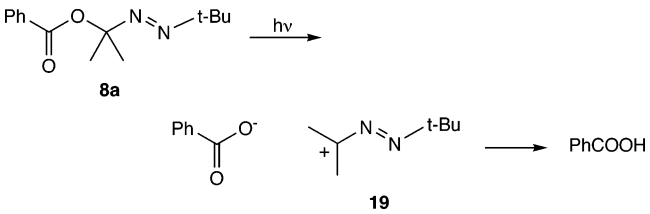
are surprisingly rapid triplet quenchers. The quenching rate constant of acetophenone triplets was in the range of 10^9 $M^{-1}s^{-1}$, which is similar to that for azo-*tert*-butane[58] and for tetramethyldiazetine dioxide quenching benzanthrone triplets.[59] The "triplet sensitized" deoxygenation of azoxybenzene[60] was shown to be a case of chemical sensitization;[61,62] that is, ketyl radicals derived from the sensitizer reduced the azoxy group.[63] For this reason, we initially suspected that our acetophenone-sensitized deoxygenation of **7Z** in toluene (cf. Table 2) followed the same pathway. However, the product distribution was unchanged in C_6D_6 solvent, suggesting that triplet sensitized deoxygenation[64] is a true photoreaction of **7Z**. In contrast, direct irradiation gave cis−trans isomerization, already a well-established process.[28,29,65] Investigating the triplet energy of azoxy compounds and the fate of oxygen are potential topics for further research.

Although the azoxy group quenches ketone triplets intermolecularly, it is inappropriate to discuss **4a**,**b** in terms of individual chromophores because the enhanced UV absorption (Table 1) indicates mixing of electronic states.[66] The experimental facts are that upon direct irradiation, neither compound undergoes deoxygenation, only **4bZ** exhibits cis−trans isomerization, and both compounds undergo inefficient α-cleavage of the benzoyl group.

Photolysis of α-Benzoyloxyazoalkanes. The initial products **8a**,**b** are themselves photolabile, giving rise to a product mixture dominated by benzoic acid and acetone. Part of the likely mechanism, shown in Scheme 2, involves the usual nitrogen loss from azoalkanes, presumably via thermolysis of the labile cis isomer[8] followed by plausible reactions of the formed *tert*-butyl and acyloxyalkyl radicals **16**. Published information on 1-acyloxyalkyl radicals is sparse and mainly concerns their inter- and intramolecular addition to alkenes.[67,68] However, Wille recently reported that photolysis of **17** gave cyclohexanone in 33% yield by fragmentation of radical **18**,[69] exactly analogous to the behavior of **16**.



The major photolysis product of **8a**,**b** is benzoic acid but Scheme 2 cannot explain its presence. In a rarely cited set of papers dating from nearly 30 years ago, Levi and Malament reported that acyclic azoalkanes containing α-chloro or α-acyloxy groups underwent heterolytic cleavage even in nonpolar solvents.[46,47] The same unusual mechanism can be applied to formation of benzoate and the known highly stabilized α-azo cation **19**.[70] Most likely,



benzoic acid arises by proton transfer from adventitious water to benzoate, as the ortho protons of the acid were clearly visible by NMR of the unopened, degassed, sealed tubes. The ionic mechanism cannot operate exclusively, even though acetone could arise when **19** traps water, because it cannot rationalize the obviously free-radical-derived products isobutane, benzaldehyde, benzophenone, and isopropyl benzoate. Thus **8a** undergoes competitive C−N homolysis and C−O heterolysis. To support the ionic mechanism, we irradiated **8a** in CD_3OD, monitoring the course of the reaction by ^1H NMR. The starting material disappeared over 19 h and gave mainly **14**, as proven by comparison with an authentic sample of the nondeuterated analogue. On further irradiation, **14** also decomposed.

Irradiation of **8b** in C_6D_6 caused azo trans−cis isomerization, in accord with the known photochemistry of phenylazoalkanes.[39] Several of the products were similar to those of **8a**, again suggesting a competition between

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ionic and homolytic decomposition. However, the yield of benzophenone and benzaldehyde from **8a** was much higher than that from **8b**, indicating that that the C−N homolysis pathway is more important in **8a** (cf. Scheme 2). The α-azo cation from **8b** is surely more stabilized than **19**, favoring ionic decomposition of **8b**.

Conclusions

Despite our failure to identify any products from **5a**, **5b**, their involvement in the photorearrangement of α-azoxy ketones **4a**, **4b*Z*** to **8a**, **8b** and their observation by ESR shows that sterically unhindered α-azoxy radicals are viable intermediates. The small hydrogen hyperfine splittings in the ESR spectrum of **5a** indicate a very high degree of resonance stabilization. Direct or acetone sensitized irradiation of **4b*Z*** also induces azoxy $Z \rightarrow E$ isomerization, but in model compound **7*Z*** acetophenone triplets cause deoxygenation without $Z \rightarrow E$ isomerization. Azoxy compounds are surprisingly rapid quenchers of acetophenone triplets. In both **4b*Z*** and **7**, steric repulsion causes thermal reversion of the *E* azoxy isomer to be much faster than in previously reported homologues. Azoesters **8a**,**b** undergo photochemical C−O heterolysis in competition with C−N homolysis to 1-acyloxy radicals, which fragment to ketones plus acyl radicals.

Experimental Section

2-*tert*-Butyl(ONN)azoxy-2-benzoylpropane, PhCOCMe$_2$−N=N(O)−Bu-t (4a). A solution of nitroso-*tert*-butane dimer (250 mg, 1.43 mmol, 0.8 equiv) in CH_3CN (10 mL) was stirred for 3.5 h at 25 °C in the dark to allow dissociation to monomer. Meanwhile, a solution of 2-benzoyl-2-aminopropane hydrochloride[71] (795 mg, 3.98 mmol, 1 equiv) in 1.5 N aq HCl (12 mL, 4.5 equiv) was added dropwise to a suspension of Ca(OCl)$_2$ (1.424 g, 5.97 mmol, 60 wt %, 1.5 equiv) in CH_2Cl_2 (24 mL) and water (24 mL) at 5 °C. After the mixture was stirred for 1 h at 5 °C, the organic layer was separated and the water layer was extracted with CH_2Cl_2 (2 × 8 mL). The combined organic phase was dried over $MgSO_4$, filtered, and concentrated to a yellow oil (0.806 g, 87% yield). The crude *N*,*N*-dichloroamine was light sensitive and was used immediately in the next step. ^{1}H NMR ($CDCl_3$) δ 8.23 (m, 2H), 7.56 (m, 1H), 7.45 (m, 2H), 1.74 (s, 6H). Following Nelson et al.,[25] KI (298 mg, 1.79 mmol) was added to the above nitroso-*tert*-butane solution at 25 °C, the temperature was lowered to 0 °C, and the *N*,*N*-dichloroamine (416 mg, 1.79 mmol) in MeCN (5 mL) was added. The mixture was stirred for 2−3 h at 5 °C, then the temperature was gradually raised to 25 °C and the mixture was stirred overnight. Water (50 mL) and ether (25 mL) were stirred in and the water layer was separated and extracted with ether (2 × 8 mL). The combined organic layer was extracted with sufficient aq $Na_2S_2O_3$ (~312 mg, 1.97 mmol) to change the color from dark brown to light green. After drying over $MgSO_4$ and removal of the solvent, the crystalline product was purified by silica gel chromatography, eluting with 4:1 hexane:ethyl acetate, R_f 0.52. Solvent evaporation yielded 273 mg (61%) of α-azoxy ketone **4a**, mp 70.5−71 °C. Further purification was effected by recrystallization from a small amount of MeOH. ^{1}H NMR ($CDCl_3$) δ 7.84 (m, 2H), 7.46 (m, 1H), 7.35 (m, 2H), 1.59 (s, 6H), 1.31 (s, 9H). NMR (C_6D_6) δ 7.99 (m, 2H), 7.08 (m, 1H), 6.99 (m, 2H), 1.64 (s, 6H), 1.07 (s, 9H). NMR (toluene-d_8) δ 7.89 (m, 2H), 7.10 (m, 1H), 7.01 (m, 2H), 1.59 (s, 6H), 1.09 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 199.7, 135.0, 132.2, 127.78, 127.72, 76.1, 68.6, 27.6, 22.5. NMR (toluene-d_8) δ 198.2, 136.0, 131.8, 128.2, 127.7, 75.8, 68.7, 27.4, 22.6.

2-Phenyl(ONN)azoxy-2-benzoylpropane (4b*Z*), PhCOCMe$_2$−N=N(O)−Ph. 2-Benzoyl-2-(*N*,*N*-dichloroamino)propane was reacted with 1.1 equiv of nitrosobenzene in MeCN as described above, except that the nitroso dimer dissociation step was omitted because nitrosobenzene exists largely as the monomer. The product was purified on silica gel, eluting with 5:1 hexane:ethyl acetate, R_f 0.43. Vacuum drying afforded 325 mg (68%) of product that was further purified by recrystallization from hot hexane (2 mL), mp 56−58 °C. ^{1}H NMR (toluene-d_8) δ 8.02 (m, 2H), 7.86 (m, 2H), 6.80−6.96 (m, 6H), 1.72 (s, 6H). ^{13}C NMR (toluene-d_8) δ 197.5, 147.3, 135.5, 132.2, 131.6, 128.7, 128.2, 127.9, 122.2, 69.6, 22.9.

2-Amino-2-phenylacetylpropane Hydrochloride, PhCH$_2$−COCMe$_2$−NH$_3$Cl. To a mixture of 3-methyl-1-phenyl-2-butene (0.7 g, 4.79 mmol) and isopentyl nitrite (0.77 mL, 5.75 mmol) cooled to 5 °C was added dropwise concentrated HCl (0.96 mL, 11.5 mmol, 12 N). After the solution was stirred for 15 min, the nitroso chloride dimer precipitated as a greenish solid. This product was washed with a small portion of warm acetone, dried in vacuo, and used in the next step without further purification. Yield 0.50 g (49%) of colorless crystals, mp 133−134 °C (lit. mp 136−137 °C).[72] The nitroso dimer (0.25 g, 1.18 mmol) was mixed with MeOH:EtOH (3 mL:3 mL) and the solution was stirred for 24 h under under 10 psi of NH_3 at 45 °C,[73] causing eventual dissolution of the dimer. The solvent was evaporated and the solid was dissolved in 50 mL of 6 M HCl by heating to 50 °C. This solution was extracted with ether, and then the aqueous phase was made alkaline with sodium carbonate (note: CO_2 evolution!). Upon raising the pH to 10, the color changed from yellow to blue/green. The precipitate was dissolved in ether and dried over Na_2SO_4, and the solvent was evaporated. The residue (190 mg) was found by NMR to be a mixture of oxime and ketone. A solution of 6 N aq HCl (10 mL) was added and the mixture was stirred for 1.5 h at 50 °C. The solvent was evaporated and the residue dissolved in a small amount of isopropyl alcohol by heating to 50 °C. The salt was precipitated by addition of ether, filtered, and dried in vacuo. Yield 91 mg (36%) of PhCH$_2$−COCMe$_2$−NH$_3$Cl, mp 134−141 °C. ^{1}H NMR (MeOH-d_4) δ 7.23−7.34 (m, 5H), 1.95 (s, 2H), 1.64 (s, 6H). ^{13}C NMR (MeOH-d_4) δ 207.0, 134.8, 130.9, 129.7, 128.3, 63.4, 43.1, 23.1.

2-*tert*-Butyl(ONN)azoxy-2-phenylacetylpropane, PhCH$_2$−COCMe$_2$−N=N(O)−Bu-t (**4c**), was prepared in the same manner as PhCO−CMe$_2$−N=N(O)−Bu-t. Purification on silica gel eluting with 4:1 hexane:ethyl acetate (R_f 0.51) yielded 32 mg of clear, oily product (42% based on PhCH$_2$−CO−CMe$_2$−NH$_3$Cl). ^{1}H NMR (toluene-d_8) δ 7.00−7.21 (m, 5H), 3.45 (s, 2H), 1.34 (s, 6H), 1.29 (s, 9H). ^{13}C NMR (toluene-d_8) δ 203.8, 137.5, 130.3, 128.4, 126.7, 76.1, 69.3, 43.5, 27.8, 21.5.

Azoxy-*tert*-butane was made according to the method of Freeman[18] and fractionally distilled twice, bp 66 °C/40 mm. ^{1}H NMR (C_6D_6) δ 1.40 (s, 9H), 1.35 (s, 9H). ^{13}C NMR (C_6D_6) δ 76.39, 57.83, 28.25, 25.69.

***tert*-Butyl(O,N,N)azoxy-2-propane**, i-Pr−N=N(O)-Bu-t,[9] was synthesized by a modified literature procedure.[74] Nitroso-*tert*-butane dimer (217.5 mg, 1.25 mmol) in absolute EtOH (2.5 mL) was stirred for 3 h at 25 °C in the dark. In a separate vessel, i-PrNHOH·HCl (290 mg, 2.6 mmol) was added in one portion to a solution of KOH (154 mg, 2.75 mmol) in absolute EtOH (2.5 mL). After brief stirring, the ethanolic suspension of i-PrNHOH was added to a dark blue solution of t-BuNO. The mixture was stirred for 2 h at 25 °C and for 16 h at 38 °C,

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after which it was diluted with 1 N aq HCl (5 mL), extracted with pentane (10 × 3 mL), and dried over Na_2SO_4. The solvent was removed by careful bulb-to-bulb distillation at 50 mmHg, cooling the receiver in a dry ice−2-propanol bath. Since the azoxyalkane product was highly volatile, some loss was unavoidable. The residue was distilled by reducing the pressure and the product was purified by preparative HPLC on a silica gel column, eluting with 10:1 pentane:ethyl ether. Bulb-to-bulb distillation at 50 mmHg removed the solvent, after which the residue was distilled at 0.001 mm to a trap at −196 °C. Yield 55 μL. GC analysis of the collected solvent indicated that it contained approximately 67 μL of i-Pr−N=N(O)Bu-t. ^{1}H NMR (C_6D_6) δ 4.32 (septet, 1H, J = 6.4 Hz), 1.36 (s, 9H), 1.15 (d, 6H, J = 6.4 Hz). ^{13}C NMR (C_6D_6) δ 75.5, 51.0, 28.1, 19.5.

t-Bu−N=N(O)−Ph (7Z) was made according to Sullivan et al.[27] and distilled, bp 44−62 °C/0.001 mm. Further purification was effected by silica gel chromatography, eluting with 9:1 hexane:EtOAc, R_f 0.54. The pure compound retains a yellow coloration. ^{1}H NMR (toluene-d_8) δ 8.13 (m, 2H), 6.90−7.02 (m, 3H), 1.47 (s, 9H). ^{13}C NMR (toluene-d_8) δ 149.6, 131.4, 128.9, 122.8, 59.2, 26.3. ^{15}N NMR (δ vs $MeNO_2$) −52.1 (N−O), −20.2. The ^{15}N HMBC experiment was optimized for a long-range N−H coupling of 3 Hz.

t-Bu−N=N(O)−Ph (7E): ^{1}H NMR (toluene-d_8) δ 6.92−7.03 (m, 3H), 6.78 (m, 2H), 0.94 (s, 9H). ^{15}N NMR (δ vs $MeNO_2$) −42.0 (N−O), 1.4.

2-Phenylazo-2-benzoyloxypropane (8b), PhCOO−C(Me)$_2$−N=N−Ph. To freshly distilled $PhNHNH_2$ (3.85 g, 35.6 mmol) and water (29 mL) at 5 °C was added acetic acid (0.95 mL, 16.6 mmol), then dropwise 5.8 mL of acetone. After the solution was stirred for 1.5 h, the air-sensitive hydrazone was quickly filtered off, washed twice with ice water, and dried in vacuo. Yield 90%. NMR (C_6D_6) δ 1.04 (s, 3H), 1.75 (s, 3H), 6.30−6.50 (br, 1H), 6.72−7.30 (m. 5H). To the freshly prepared hydrazone (1.446 g, 9.77 mmol) in CH_2Cl_2 (8 mL) at −78 °C was added dropwise t-BuOCl (1.219 g, 11.24 mmol). The mixture was stirred for 2.5 h as the temperature rose to 25 °C. The solvent and *tert*-butyl alcohol byproduct were evaporated and the residual Ph−N=N−CMe_2−Cl was dissolved in benzene (5 mL). Because neat Ph−N=N−CMe_2−Cl decomposes within 30 min at 25 °C, this freshly prepared solution was added dropwise to silver benzoate (1.79 g, 7.80 mmol) in benzene (10 mL) at 5 °C. The heterogeneous mixture was stirred for 1 h at 5 °C, then at 25 °C for 3 days. The azoester suspension was filtered through a cotton plug and then through filter paper and the filtrate was concentrated to a deep yellow oil. The crude product was purified on silica gel, eluting with 9:1 hexane/ethyl acetate, R_f 0.47. Yield 1.71 g (81%) of deep yellow solid with mp 48−49 °C. The compound crystallized from hexane after maintaining the solution at −20 °C for several weeks. ^{1}H NMR (C_6D_6) δ 8.26 (m, 2H), 7.79 (m, 2H), 7.03−7.16 (m, 6H), 1.78 (s, 6H). ^{13}C NMR (C_6D_6) δ 165.3, 152.3, 133.2, 132.2, 131.4, 130.5, 129.5, 128.9, 123.4, 102.6, 25.2.

2-*tert*-Butylazo-2-benzoyloxypropane, PhCOO−CMe$_2$−N=N−Bu-t (8a). Crude 2-*tert*-butylazo-2-chloropropane, t-Bu−N=N−CMe_2−Cl,[75] was treated with silver benzoate as in the synthesis of **8b** above. The product was purified on silica gel, eluting with 9:1 hexane:ethyl acetate, R_f 0.48. Yield 0.956 g (53% from acetone−*tert*-butyl hydrazone). The azo compound crystallized at 25 °C over time, yielding ice-like, transparent crystals that melted at 29−30 °C to a light beige oil. ^{1}H NMR (C_6D_6) δ 8.20−8.22 (m, 2H), 7.02−7.12 (m, 3H), 1.65 (s, 6H), 1.20 (s, 9H). ^{13}C NMR (C_6D_6) δ 164.75, 132.67, 132.02, 130.04, 128.42, 101.32, 67.09, 26.69, 24.59.

2-*tert*-Butylazo-2-methoxypropane, t-Bu−N=N−C(Me)$_2$−OMe (protiated 14).[76] To t-Bu−N=N−CMe_2−Cl (0.934 g, 7.29 mmol) prepared as above and cooled to −78 °C was added 2 mL of MeOH.[77] In a separate vessel, sodium methoxide (0.45 g, 8.39 mmol) was dissolved in MeOH (4 mL) and the solution was added to the reaction mixture dropwise at −78 °C. The mixture was stirred at −78 °C for 10 min and the temperature was allowed to increase gradually to 25 °C over 3 h. Water and CH_2Cl_2 were added, the mixture was shaken, and the aqueous phase was extracted with CH_2Cl_2 several times. The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated. Removal of residual solvent in vacuo at ∼40 mmHg yielded 0.509 g (44% from t-Bu−NH−N=CMe_2) of volatile liquid. ^{1}H NMR (MeOH-d_4) δ 3.39 (s, 3H), 1.21 (s, 6H), 1.19 (s, 9H).

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Supporting Information Available: Calculated isotropic Fermi contact couplings for **5a**, ESR spectra of **5a**, UV spectra of **4a**, **6**, **8a**, **4bZ**, **7Z**, and **8b**, computed structures of **15**, **8**, **5a**, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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