# Reaction of 1,2-Dioxetanes with Heteroatom Nucleophiles: Adduct Formation by Nucleophilic Attack at the Peroxide Bond

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**Abstract:** The reactions of 3,3-disubstituted 1,2-dioxetanes **1** with numerous heteroatom nucleophiles, e.g., $R_2NH$, $R_3N$, RSH, $R_2S$, $CN^-$, $SCN^-$, $Br^-$, $Cl^-$, $OH^-$, and $O_2^{\bullet-}$, were investigated. Initial nucleophilic substitution at the sterically less hindered site of the dioxetane peroxide bond leads to addition, deoxygenation, and fragmentation products. The observed $S_N2$ chemistry was substantiated with the dioxetane **1c** because bromide ion displacement by the proximate alkoxide ion site afforded epoxide products. Thus, with anionic nucleophiles the epoxy alcohol **8c** was obtained in appreciable amounts, and triethylamine and DABCO gave with **1c** exclusively the alkoxyammonium epoxides **4c** and **5c**. Moreover, the labile alkoxysulfonium epoxide **6c** was detected as an intermediate in the deoxygenation of **1c** by diphenyl sulfide. From the reaction of **1b–d** with secondary amines were isolated the hydroxylamine derivatives **2** and **3**, and the cyanide and thiocyanate ions gave with **1c,d** five-membered-ring insertion products, namely, the carbonates **9c,d** and the cyclic sulfite **10c**.

## Introduction

On account of their unique property to generate electronically excited carbonyl fragments on thermolysis, 1,2-dioxetanes have received a great deal of attention during the last decades.[1] Astonishingly, the chemical behavior of these peroxides has only scarcely been studied. To date, the most important transformations of dioxetanes with nucleophiles are their deoxygenation by phosphines[2] and sulfides[3] into epoxides and the reduction by lithium aluminum hydride,[4] thiols,[5] and biologically relevant reductands[6] to give diols. Other electron donors such as enol ethers, amines,[7] or electron-rich arenes[8a,b] react with simple tetrasubstituted dioxetanes to undergo cleavage into the corresponding carbonyl products with (CIEEL mechanism[8c]) or without light emission (dark decomposition[7]). For this decomposition route and for dioxetanes which bear electron-donating substituents,[8d,e] an electron-transfer mechanism operates.

Recently we reported the novel reactions of electron-rich olefins,[9a] enamines,[9b] and alkyllithium reagents[10] with 3,3-disubstituted 1,2-dioxetanes. Since reactions between peroxides[11] or peroxy esters and easily oxidized nitrogen and sulfur compounds are of current interest,[12] because they react either by the traditionally accepted nucleophilic substitution mechanism ($S_N2$) or by the recently popular electron-transfer mechanism (SET),[13] we decided to differentiate between these mechanistic alternatives in the case of dioxetanes, by introducing halomethyl-substituted dioxetanes as mechanistic probes.[10] Consequently, we examined the reaction of 3-(bromomethyl)-3-phenyl-1,2-dioxetane (**1c**) with a series of heteroatom nucleophiles, which include secondary and tertiary amines, sulfur derivatives, and anionic species such as $CN^-$, $SCN^-$, $X^-$ (Cl, Br), $HO^-$, and the radical anion $O_2^{\bullet-}$ (Scheme I). For comparison, the dioxetanes **1a,b,d** were treated with some of the nucleophiles.

## Results

**Reaction of Dioxetanes 1b–d with Secondary Amines.** All reactions of the dioxetanes **1b–d** with diisopropylamine and morpholine (Table I, entry 1; Table II, entries 2–5) afforded the corresponding β-hydroxyalkoxyamines **2** and **3** (Scheme I) as main products. These were fully characterized, with the exception of adduct **2c**, which decomposed during isolation, and therefore, its structure assignment rests only on $^1H$ and $^{13}C$ NMR and IR spectral data. Especially in the mechanistically most significant example, namely, the reaction of the dioxetane **1c** with diisopropylamine, only traces of the cleavage product ω-bromoacetophenone (**12c**) were observed by $^1H$ NMR spectroscopy (Table I, entry 1); no epoxide products could be detected.

**Reaction of Dioxetanes 1a,c,d with Tertiary Amines.** When dioxetanes **1a,d** were treated with equimolar amounts of triethylamine in methylene chloride at −20 °C, an essentially instantaneous reaction occurred, and by $^1H$ NMR spectroscopy the dioxetane cleavage products acetophenone (**12a**) and 1,3-diphenylacetone (**12d**) were observed exclusively. Moreover, even with catalytic amounts of triethylamine, the dioxetane was consumed within 30 min.

When dioxetane **1c** was allowed to react with equimolar amounts of triethylamine, the novel alkoxyammonium bromide **4c** was obtained exclusively (Table I, entry 2). Due to its thermal lability and highly hygroscopic nature, **4c** could not be purified.

Similar results were obtained when **1c** was treated with 1,4-diazabicyclo[2.2.2]octane (DABCO) in $CDCl_3$ at −20 °C. Again, the dioxetane was consumed essentially instantaneously with exclusive formation of the DABCO adduct **5c** (Table I, entry 3). The latter was even more labile than **4c**.

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Scheme I

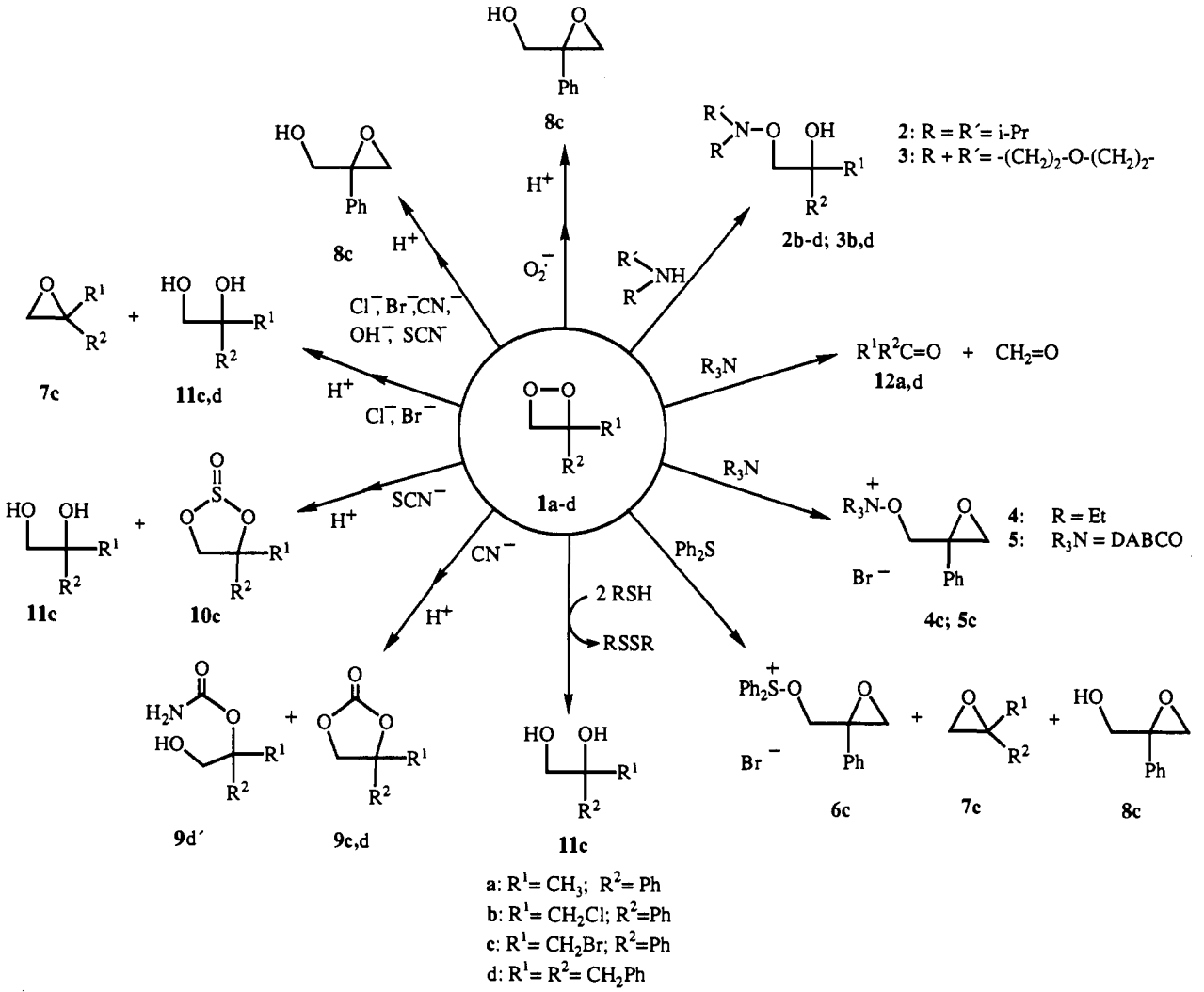



Table I. Reactions of Dioxetane **1c** with Heteroatom Nucleophiles

| | | reactn conditns | | | product distribution[a] | | | | | mass |
|---|---|---|---|---|---|---|---|---|---|---|
| entry | nucleophile | solvent | temp (°C) | time (h) | addn[b] | epoxidn **8c** | redn **11c** | deoxygenn **7c** | fragn[c] **12c** | balance (%) |
| 1 | $(i\text{-Pr})_2NH$ | $CDCl_3$ | 0 | 0.2 | 99 (**2c**) | – | – | – | 1 | >95[d] |
| 2 | $Et_3N$ | $CH_2Cl_2$ | −20 | 0.5 | 100 (**4c**) | – | – | – | – | 92[e] |
| 3 | DABCO | $CH_2Cl_2$ | −20 | 0.1 | 100 (**5c**) | – | – | – | – | >95[d] |
| 4 | PhSH | $CH_2Cl_2$ | −20 | 0.2 | – | – | 78 | – | 22 | 91[d] |
| 5 | $PhCH_2SH$ | $CDCl_3$ | −20 | 0.2 | – | – | >99 | – | <1 | 95[d] |
| 6 | $Ph_2S$ | $CDCl_3$ | −20 | 0.5 | 11 (**6c**) | 20 | – | 66 | 3 | 91[d] |
| 7 | $CN^-$ | $CH_3CN/H_2O$ | 0 | 0.1 | 88 (**9c**) | 12 | – | – | – | 77[f] |
| 8 | $SCN^-$ | $CH_3CN/H_2O$ | 0 | 0.1 | 58 (**10c**) | 15 | 26 | – | – | 86[f] |
| 9 | $Br^-$ | $CH_3CN/H_2O$ | 0 | 0.5 | – | 79 | 11 | 10 | – | 88[e] |
| 10 | $Cl^-$ | $CH_3CN/H_2O$ | 0 | 24 | – | 27 | 70 | 3 | – | 92[e] |
| 11 | $OH^-$ | MeOH | −10 | 1 | – | 100 | – | – | – | 92[e] |
| 12 | $O_2^{\bullet-}$ | $CH_3CN$ | 0 | 0.25 | – | 100 | – | – | – | 93[e] |

[a] Normalized to 100%; determined by $^1H$ NMR; 100% conversion of the dioxetane. [b] The type of adduct is specified in parentheses. [c] Detection of $CH_2{=}O$ was not attempted. [d] Determined by quantitative $^1H$ NMR (hexamethyldisiloxane as standard). [e] Determined gravimetrically. [f] Isolated yield of pure products.

**Reactions of Dioxetane 1c with Sulfur Nucleophiles.** The reduction of dioxetane **1c** by thiophenol gave the expected diol **11c**, which was obtained together with minor amounts of ω-bromoacetophenone (**12c**), i.e., **11c**:**12c** = 78:22. In the case of benzyl mercaptan, the diol **11c** was formed essentially exclusively, with only traces of the ω-bromoacetophenone (**11c**:**12c** = >99:<1). No epoxide products and no acetophenone (dehalogenation) could be observed by $^1H$ NMR spectroscopy.

For the reaction of dioxetane **1c** with diphenyl sulfide, the $^1H$ NMR spectrum of the crude reaction mixture revealed small amounts (3%) of cleavage product **12c**, epoxide **7c** as the major product (66%), and epoxy alcohol **8c** (20%).[14]

Important, from the mechanistic point of view, was the observation of the sulfonium adduct **6c** (11% yield). Due to its thermal lability, the structural assignment of **6c** rests merely on $^1H$ NMR data. Like the ammonium salts **4c** and **5c**, **6c** also shows

(14) A sample of epoxide **7c** was prepared independently by dimethyldioxirane epoxidation[15] of 1-bromo-2-phenyl-2-propene; treatment of the same olefin with $H_2O_2$/HCOOH afforded diol **11c**, which on base-catalyzed cyclization gave epoxy alcohol **8c** (Heil, M. Dissertation, University of Würzburg, 1992).

**Table II.** Reactions of Dioxetanes **1a,b,d** with Heteroatom Nucleophiles

| entry | dioxetane | nucleophile | reactn conditns: solvent | temp (°C) | time (h) | yield[a] (%) | mass balance[b] (%) |
|---|---|---|---|---|---|---|---|
| 1 | **1a** | $Et_3N$ | $CH_2Cl_2$ | −20 | 0.1 | 98 (**12a**) | 98 |
| 2 | **1b** | $(i\text{-}Pr)_2NH$ | $CH_2Cl_2$ | 0 | 0.5 | 84 (**2b**) | 90 |
| 3 | **1b** | morpholine | $CH_2Cl_2$ | 0 | 0.5 | 65 (**3b**), 9 (**12b**) | 74 |
| 4 | **1d** | $(i\text{-}Pr)_2NH$ | $CH_2Cl_2$ | 0 | 15 | 41 (**2d**) | 90[c] |
| 5 | **1d** | morpholine | $CH_2Cl_2$ | 0 | 15 | 74 (**3d**), 12 (**12d**) | 86 |
| 6 | **1d** | $Et_3N$ | $CH_2Cl_2$ | −20 | 0.1 | 96 (**12d**) | 96 |
| 7 | **1d** | $CN^-$ | $CH_3CN/H_2O$ | 0 | 1 | 71 (**9d**), 15 (**9d'**) | 86 |
| 8 | **1d** | $Br^-$ | $CH_3CN/H_2O$ | 0 | 6 | 68 (**11d**) | 88 |
| 9 | **1d** | $Cl^-$ | $CH_3CN/H_2O$ | 0 | 96 | no reaction | 90[d] |

[a] 100% conversion of the dioxetanes; products are given in parentheses. [b] Determined gravimetrically and by $^1H$ NMR; dioxetane cleavage products were not isolated in every case. [c] 50% of dioxetane cleavage product **12d** was detected by $^1H$ NMR. [d] Recovered **1d**.

a characteristic AB pattern ($^1H$ NMR) at the low-field value for the $CH_2OS^+$ moiety at $\delta$ = 4.86 and 5.71 with a coupling constant of $J_{AB}$ = 12.4 Hz. These signals, as well as the corresponding ones for the epoxide, disappeared completely when the sample was kept at −20 °C for 1 h.

**Reactions of Dioxetanes 1c,d with Anionic Nucleophiles.** The transformations of dioxetanes **1c,d** with potassium cyanide gave carbonates **9c,d**, epoxy alcohol **8c**, and carbamic acid ester **9d'** essentially instantaneously (Tables I and II, entries 7). The hitherto unknown carbonates **9c,d** were fully characterized, easily identified by their typical C=O stretching frequencies in the IR spectra.[16] The assigned regiochemistry of the carbamate **9d'** was confirmed by the coupling of the hydroxy proton with the neighboring methylene group in the $^1H$ NMR spectrum.

A control experiment showed that an aqueous solvent system is essential for adduct formation in the reaction of the cyanide ion with the dioxetane. Thus, when dioxetane **1c** was treated with potassium cyanide in $CDCl_3$ under phase-transfer conditions, other than unidentified products and epoxy alcohol **8c**, mostly cleavage of **1c** into **12c** (**8c**:**12c** = 69:31) was observed by $^1H$ NMR spectroscopy.

As in the case of the cyanide adducts, the dioxetane **1c** was converted with potassium thiocyanate to a ring-expanded adduct, namely, the cyclic sulfite **10c**. The previously unknown **10c** was obtained as a mixture of diastereomers (*dr* = 55:45), which was fully characterized spectrally.[17] Furthermore, 36% of a mixture of epoxy alcohol **8c** and diol **11c** (**8c**:**11c** = 37:63) was isolated.

In the advantageous aqueous acetonitrile solvent system, dioxetanes **1c** and **1d** were reduced as well by halide ions. Dioxetane **1c** with potassium bromide afforded a mixture of epoxy alcohol **8c**, diol **11c**, and epoxide **7c** (deoxygenation) in 92% yield (Table I, entry 9). The reaction of dioxetane **1c** with KBr in deuteriochloroform caused mostly decomposition of the dioxetane, with appreciable formation of epoxy alcohol **8c** and unidentified products.

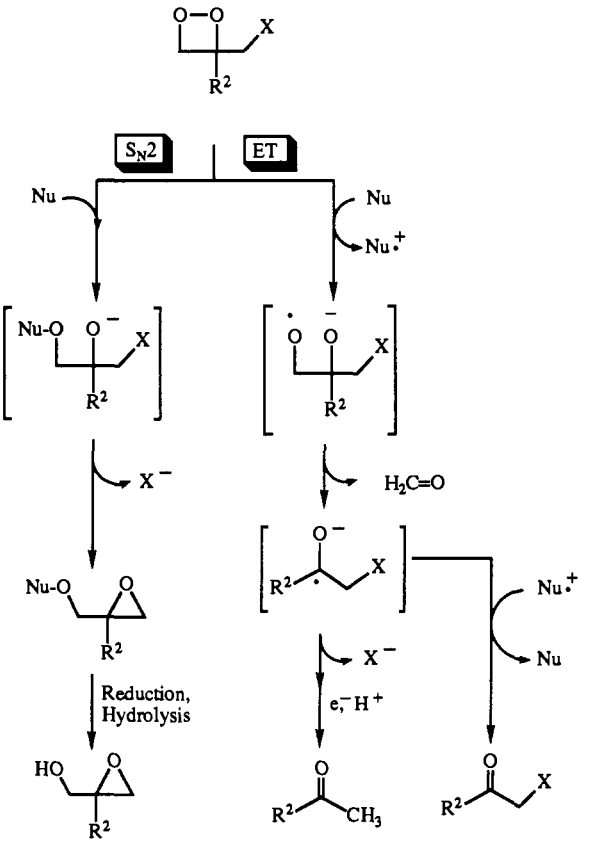
The same products were obtained when dioxetane **1c** was exposed to KCl in aqueous $CH_3CN$ (**8c**:**10c**:**7c** = 27:70:3), but a longer reaction time was necessary (Table I, entry 10). While dioxetane **1d** was reduced by potassium bromide to yield diol **11d** and only a small amount of cleavage product **12d** (**11d**:**12d** = 88:12), no reaction was observed with KCl (Table II, entries 8 and 9).

Epoxy alcohol **8c** was the only product when dioxetane **1c** was treated with methanolic KOH (Table I, entry 11). Furthermore, epoxy alcohol **8c** was formed exclusively in the reaction of dioxetane **1c** with $KO_2$ in dry acetonitrile (Table I, entry 12).

## Discussion

Our product studies on the reaction of dioxetanes **1a–d** with different heteroatom nucleophiles provide compelling evidence for

**Scheme II**




an initial nucleophilic attack ($S_N2$ mechanism) at the peroxide bond of the dioxetane. The formation of epoxides was rationalized in terms of nucleophilic attack at the less hindered side of the peroxide bond and subsequent intramolecular halide ion displacement by the proximate alkoxide nucleophile (Scheme II). Alternatively, electron transfer to the dioxetane would generate a dioxetane radical anion, which should undergo fragmentation into formaldehyde and a ketyl radical faster than intramolecular halide displacement. The ketyl radical would, on electron back-transfer, yield the dioxetane cleavage product or would, on halide elimination, eventually yield dehalogenated ketone[18] (Scheme II).

In the $S_N2$ mechanism (Scheme III) the bona fide primary intermediate is the nucleophile–dioxetane adduct with a proximate alkoxide function, from which all products observed in the reaction of the dioxetanes **1a–d** with the various nucleophiles can be rationalized. The reaction of dioxetanes **1b–d** with secondary amines leads to the stable N,N,O-trisubstituted hydroxylamines **2** and

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(17) Ibid., p 295.

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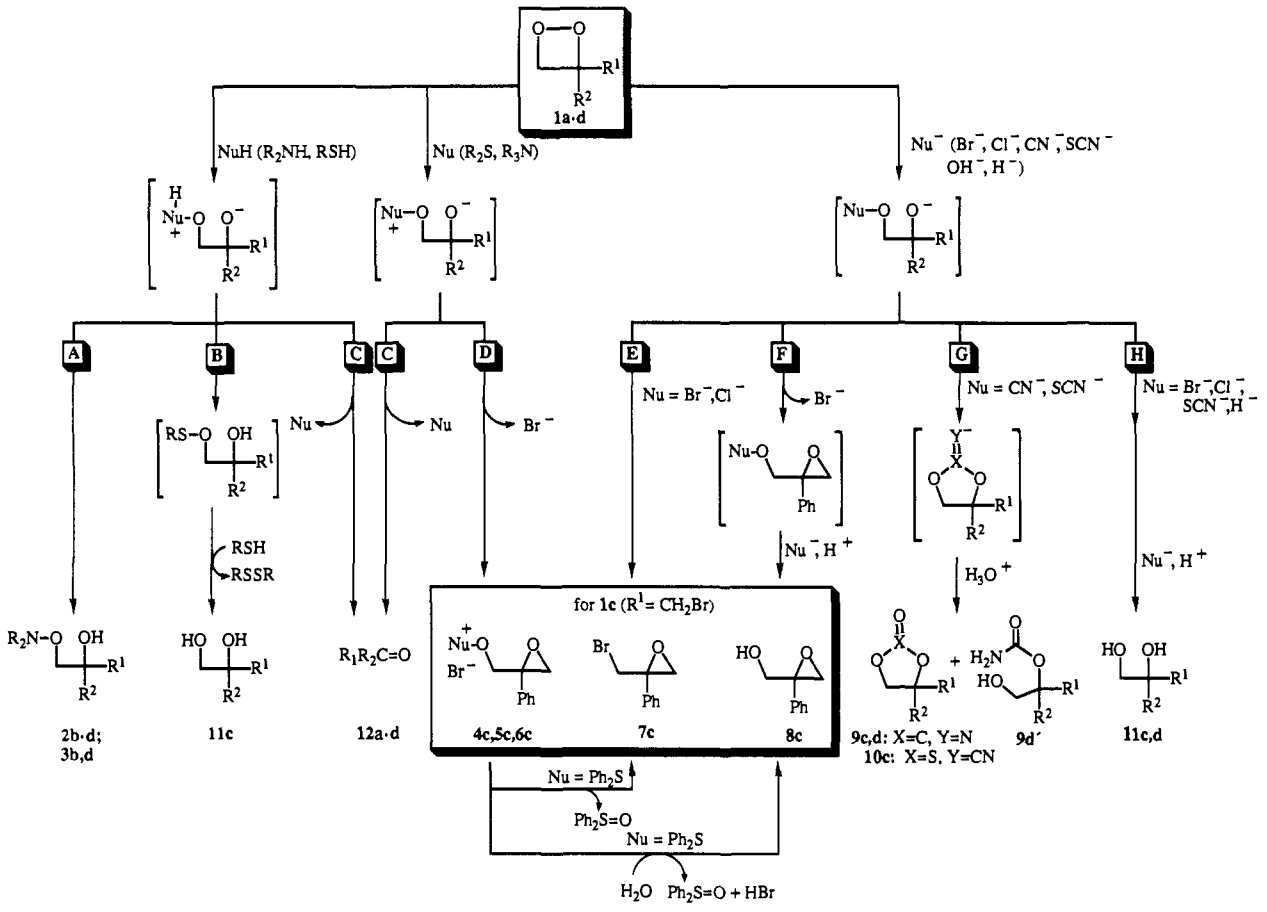
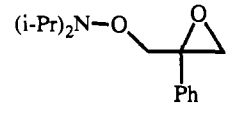
**Scheme III**




3. Such stable adducts, which are well documented for the reaction of secondary amines with diacyl peroxides,[19] are not observed for dialkyl peroxides and are novel for dioxetanes.



**13**

Unfortunately, the lack of epoxide **13** formation (Table I, entry 1) in the reaction of dioxetane **1c** with diisopropylamine through bromide elimination by the proximate alkoxide ion does not allow differentiation between SET and $S_N2$ character (Scheme II). Nevertheless, an initial SET step should lead to substantial amounts of cleavage products (Scheme II), while in fact only traces were detected for dioxetane **1c** (Table I, entry 1). This speaks for pronounced $S_N2$ character of the reactions of dioxetanes **1** with $R_2NH$; besides, the formation of cleavage products can also be explained by Grob fragmentation[20] of the intermediary 1,5-zwitterion (Scheme III, path C). Nevertheless, the dominant course of the initially formed zwitterion is fast irreversible proton transfer from the ammonium site to the alkoxide ion of **3** (Scheme III, path A).

For tertiary amines, which cannot readily deactivate the 1,5-zwitterion by proton transfer, we anticipate different chemical behavior. For example, dialkyl peroxides[21] and endoperoxides,[22] which bear $\alpha$-H atoms, usually yield alcohols and ketones through base-catalyzed fragmentation, the so-called Kornblum–De La Mare rearrangement.[21b,23] Although there have been precedents for the amine-catalyzed conversion of dioxetanes into $\alpha$-hydroxy carbonyl products, namely, in the decomposition of enamine dioxetanes,[24] such base-catalyzed fragmentation of dioxetane **1c** by triethylamine or DABCO was not observed here. The most effective deactivation of the initially formed zwitterion is internal nucleophilic attack by the proximate alkoxide site to displace $Br^-$ and afford the bromide salts **4** and **5** (Scheme III, path D). Similar (acyloxy)ammonium salts were postulated as primary products in diacyl peroxide/tertiary amine reactions;[25] however, only in a few cases could these adducts be isolated or spectroscopically detected.[26] When internal halide ion elimination is not possible, as in the case of dioxetanes **1a,d**, the zwitterion intermediate suffers Grob fragmentation[20] to yield exclusively the corresponding cleavage products **12a,d** (Scheme III, path C).

Since single-electron-transfer (SET) chemistry has been reported,[26a,27] for the reaction of diacyl peroxides and peroxy esters with tertiary amines, the amines employed in our investigations, namely, triethylamine and DABCO,[28,29] should have been well-suited for exposing the electron-transfer behavior of dioxetanes. Nevertheless, the electron-transfer-initiated cleavage of dioxetane

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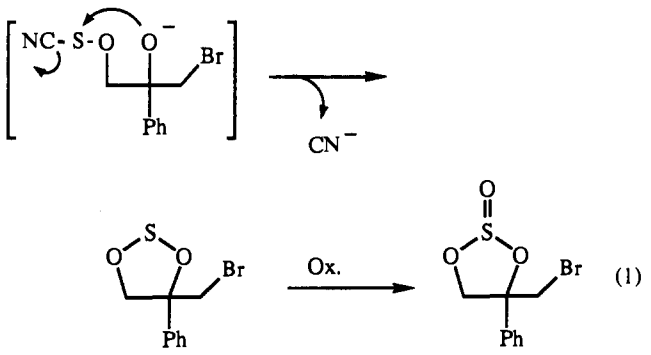
**1c** by triethylamine or DABCO (Scheme II) and subsequent dehalogenation were not observed (Table I, entries 2 and 3).

As expected, the corresponding 1,2-diol **11c** was formed in high yields when dioxetane **1c** was allowed to react with thiophenol and benzyl mercaptan (Table I, entries 4 and 5). However, in view of the results obtained for the reaction of dioxetanes **1** with amines, we propose also an $S_N2$ mechanism for this reduction. The resulting intermediary zwitterion gives first, on proton transfer, the labile sulfenic acid ester, and the latter is readily converted to the diol by subsequent attack of a second thiol molecule (Scheme III, path B).

In contrast to amines, sulfides deoxygenate dioxetanes to afford epoxides and sulfoxides under conditions of oxygen atom transfer.[3,30] To these deoxygenations was attributed a $S_N2$ mechanism.[3a,30a] Indeed, the labile *S*-alkoxysulfonium salt **6c** was obtained in the reaction of dioxetane **1c** with diphenyl sulfide. Unlike mercaptans, which deactivate the zwitterion by proton transfer toward competing alternative transformations, in the case of sulfides, the primary zwitterion undergoes bromide elimination to generate the sulfonium epoxide **6c** (Scheme III, path D). While the corresponding tertiary amine adducts **4c** and **5c** are persistent, **6c** readily suffers bromide ion attack to generate the epoxide **7c** as the observed main product. Alternatively, the easily hydrolyzed alkoxysulfonium salt **6c** is converted to the epoxy alcohol **8c** by adventitious water.[31] The small amounts of the cleavage product **12c** (Table I, entry 6) could derive from Grob fragmentation[20] of the initially formed zwitterion.

The carbonates **9c,d** and the sulfite **10c**, which were obtained from the reaction of dioxetanes **1c,d** with cyanide and thiocyanate (Table I, entries 7 and 8; Table II, entry 7), are proposed to arise from nucleophilic attack of the anion on the dioxetane peroxide bond (Scheme III, path G). In the case of the cyanide adduct, attack of the proximate alkoxide ion site on the cyanate functionality would lead to a cyclic imine, which on acidic workup is readily hydrolyzed to yield either the carbonates **9c,d** or the carbamate **9d'**. In the case of sulfite **10c**, the cyanide ion is eliminated instead by reaction at the electrophilic sulfur[32a] to afford a cyclic sulfoxylate (eq 1). The labile sulfoxylates, however, are readily oxidized to yield sulfites.[32b,c]




(1)

**10c**

With cyanide, as well as with thiocyanate, the epoxy alcohol **8c** was obtained as a side product in the reaction with dioxetane **1c** (Table I, entries 7 and 8). As in the case of the amine and sulfide reactions, this can be explained in terms of bromide elimination by the proximate alkoxide ion in the initially formed zwitterion (Scheme III, path F) and hydrolysis of the resulting unstable adducts.

Since the bromide ion has a nucleophilicity[33] and oxidation potential[33a] similar to those of the cyanide or thiocyanate ions, it was anticipated that $Br^-$ should attack the dioxetane peroxide bond to give the zwitterion as a nucleophile adduct. This was confirmed by the formation of the diol **11c**, the epoxy alcohol **8c**, and the epoxide **7c** (Table I, entries 9 and 10) when dioxetane **1c** was treated with $Br^-$ or $Cl^-$ (Scheme III, paths E, F, and H). In fact, Richardson[34] observed an accelerated decomposition of 3,3-dimethyl-1,2-dioxetane by bromide ion and interpreted it in terms of nucleophilic attack of $Br^-$ on the peroxide bond. Furthermore, oxidations of halides by diacyl[35] and sulfonyl peroxides[36] are known to proceed through intermediary hypohalites.

The initially produced zwitterion with the hypohalite functionality, derived from the attack of $Br^-$ or $Cl^-$ at the peroxide bond of dioxetane **1c**, has three options to transform into stable products: (i) elimination of the hypohalite anion by attack of the proximate alkoxide ion (dehalogenation) to afford epoxide **7c** (Scheme III, path E), (ii) analogous bromide elimination followed by subsequent dehalogenation of the hypohalite functionality[37] with formation of epoxide **8c** (Scheme III, path F), and (iii) fast protonation of the proximate alkoxide ion center with subsequent hypohalite reduction[37] to generate diol **11c** (Scheme III, path H). These three reaction modes are exhibited by dioxetane **1c** when treated with $Br^-$ and $Cl^-$ (Table I, entries 9 and 10).

The quantitative conversion of dioxetane **1c** with hydroxide ion to afford epoxy alcohol **8c** (Table I, entry 11) is also rationalized to proceed in terms of nucleophilic attack of hydroxide ion on the dioxetane peroxide bond, as suggested for the reduction of dialkyl peroxides by $HO^-$.[38] However, only one case of such a reduction of dioxetanes by $HO^-$ has been reported.[34]

Elimination of the bromide ion (Scheme III, path F) would result in an epoxy hydroperoxide. Since hydroperoxides are known to undergo facile reduction under alkaline conditions[4] to yield alcohols, this sequence constitutes a reasonable rationale for the quantitative production of epoxy alcohol **8c** from dioxetane **1c** on exposure to NaOH (Scheme III, path F).

Epoxy alcohol **8c** is the only product (Table I, entry 12) in the reaction of dioxetane **1c** with potassium superoxide, one of the most potent nucleophiles.[39] This is analogous to the reaction of the superoxide ion[40] with diacyl peroxides,[41] dialkyl peroxides,[38] and endoperoxides.[42] Again, nucleophilic displacement on the peroxide bond by $O_2^{\bullet-}$ was discussed as a likely mechanism.[38,40]

To summarize, the reaction of the 3,3-disubstituted 1,2-dioxetanes **1** with a large number of heteroatom nucleophiles establishes the $S_N2$ reactivity of these strained peroxides. The sterically exposed oxygen of the dioxetane peroxide bond becomes the site of nucleophilic attack to produce an anionic or zwitterionic adduct. Numerous reaction channels become available to the intermediates, which depend on their chemical nature. These include addition, deoxygenation, reduction, and fragmentation products. Particularly valuable as a mechanistic tool to substantiate the observed $S_N2$ chemistry was the bromomethyl-substituted dioxetane **1c**. Debromination through internal nucleophilic displacement by the resulting proximate alkoxide ion site constitutes the mechanistic diagnosis for $S_N2$ reactivity of these electrophilic peroxides.

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## Experimental Section

**General Aspects.** For common analytical instruments and spectral calibrations, cf. ref 30b. Column chromatography: silica gel (63–200-μm particle size) from Woelm as the stationary phase with an adsorbance/substrate ratio of about 80:1. Dioxetanes **1a–d**[10] were prepared according to the literature procedure by NaOH-catalyzed cyclization of the corresponding β-bromo hydroperoxides.

**CAUTION!** *3,3-Disubstituted 1,2-dioxetanes are hazardous compounds, especially when handled in neat form.*

**Reaction of Dioxetanes 1b–d with Secondary Amines. General Procedure.** A ca. 0.1 M solution of the dioxetane in methylene chloride was cooled to 0 °C, and equimolar amounts of diisopropylamine or morpholine were added in 2 mL of methylene chloride. After total conversion of the dioxetane (negative KI test), the solvent was removed at 20 °C/15 Torr. The composition of the crude product mixture was determined by $^1$H NMR spectroscopy, and the products were separated and purified by column chromatography.

**Reaction of Dioxetanes 1b–d with Diisopropylamine. Dioxetane 1b.** Dioxetane **1b** (106 mg, 0.574 mmol) was treated with diisopropylamine (60.0 mg, 0.593 mmol) in 7 mL of $CH_2Cl_2$, and within 15 min **2b** and **12b** were formed in a ratio of 96:4 (mass balance >90%). By chromatography (3:1 methylene chloride/ethyl acetate as eluent) there was isolated 140 mg (84%) of **2b** as a colorless oil.

***N*-[(3-Chloro-2-hydroxy-2-phenylpropyl)oxy]-*N*,*N*-diisopropylamine (2b):** $^1$H NMR ($CDCl_3$, 250 MHz) δ 1.02 (d, $J$ = 6.4 Hz, 6 H, $CH_3$), 1.03 (d, $J$ = 6.4 Hz, 6 H, $CH_3$), 3.09 (sept, $J$ = 6.4 Hz, 2 H, $(CH_3)_2CH$), 3.10 (br s, 1 H, OH), AB pattern ($\delta_A$ = 3.91, $\delta_B$ = 3.97, $J$ = 11.2 Hz, 2 H, $CH_2O$ or $CH_2Cl$), AB pattern ($\delta_A$ = 3.98, $\delta_B$ = 4.04, $J$ = 1.0 Hz, 2 H, $CH_2O$ or $CH_2Cl$), 7.29–7.52 (m, 5 H, arom H); $^{13}$C NMR ($CDCl_3$, 50 MHz, −20 °C) δ 16.2, 17.9, 20.8, 21.0 (all q, $CH_3$), 50.5 (t, $CH_2Cl$) 53.1 and 53.4 (d, $(CH_3)_2CH$), 75.4 (s), 78.6 (t, $CH_2O$), 125.3 (d), 127.8 (d), 128.1 (d), 140.4 (s); IR ($CCl_4$) 3600, 3090, 3060, 3010, 2970, 2900, 1510, 1460, 1395, 1350 cm$^{-1}$; mass calcd for $C_{15}H_{24}ClNO_2$ ($M^{\cdot+}$) 285.1496, found 285.1497.

**Dioxetane 1c.** A solution of dioxetane **1c** (27.3 mg, 0.119 mmol) in 0.3 mL of $CDCl_3$ was cooled to 0 °C, and a solution of diisopropylamine (12.2 mg, 0.121 mmol) in 0.3 mL of $CDCl_3$ was added to it. After 10 min the reaction mixture was submitted to $^1$H NMR analysis, which showed the total conversion of the dioxetane to yield adduct **2c** and ω-bromoacetophenone (**12c**) in a ratio of 99:1 (mass balance >95%). On evaporation of the solvent at 0 °C/15 Torr, the product decomposed into a yellow oil, which consisted of a complex product mixture according to $^1$H NMR and TLC.

***N*-[(3-Bromo-2-hydroxy-2-phenylpropyl)oxy]-*N*,*N*-diisopropylamine (2c):** $^1$H NMR ($CDCl_3$, 200 MHz) δ 1.00 (d, $J$ = 6.4 Hz, 6 H, $CH_3$), 1.03 (d, $J$ = 6.4 Hz, 6 H, $CH_3$), 3.05 (br s, 1 H, OH), 3.08 (sept, $J$ = 6.4 Hz, 2 H, $(CH_3)_2CH$), AB pattern ($\delta_A$ = 3.81, $\delta_B$ = 3.88, $J$ = 10.5 Hz, 2 H, $CH_2Br$), AB pattern ($\delta_A$ = 4.00, $\delta_B$ = 4.05, $J$ = 11.1 Hz, 2 H, $CH_2O$), 7.25–7.50 (m, 5 H, arom H); $^{13}$C NMR ($CDCl_3$, 50 MHz, −20 °C) δ 15.9, 17.9, 20.7, 20.9 (all q, $CH_3$), 44.3 (t, $CH_2Br$), 53.0 and 53.2 (d, $(CH_3)_2CH$), 74.8 (t, $CH_2O$), 79.0 (s), 125.0 (d), 127.7 (d), 128.0 (d), 140.5 (s); IR ($CDCl_3$) 3560, 3080, 3040, 2990, 2890, 1600, 1450, 1380, 1180, 1060 cm$^{-1}$.

**Dioxetane 1d.** Dioxetane **1d** (153 mg, 0.637 mmol) and diisopropylamine (72.0 mg, 0.711 mmol) in 7 mL of $CH_2Cl_2$ gave within 15 h **2d** and **12d** in a ratio of 50:50 (mass balance >90%). By chromatography (5:1 methylene chloride/ethyl acetate as eluent) 89.0 mg (41%) of **2d** was isolated as a colorless oil.

***N*-[(2-Benzyl-2-hydroxy-3-phenylpropyl)oxy]-*N*,*N*-diisopropylamine (2d):** $^1$H NMR ($CDCl_3$, 250 MHz) δ 0.95 (d, $J$ = 12.5 Hz, 12 H, $CH_3$), 2.28 (br s, 1 H, OH), AB pattern ($\delta_A$ = 2.69, $\delta_B$ = 2.83, $J$ = 13.9 Hz, 4 H, $CH_2Ph$), 3.01 (sept, $J$ = 6.3 Hz, 2 H, $(CH_3)_2CH$), 3.53 (s, 2 H, $CH_2O$), 6.97–7.25 (m, 10 H, arom H); $^{13}$C NMR ($CDCl_3$, 50 MHz, −20 °C) δ 17.1 and 20.9 (q, $CH_3$), 43.5 (t, $CH_2Ph$), 53.2 (d, $(CH_3)_2CH$), 74.4 (t, $CH_2O$), 80.1 (s), 126.2 (d), 127.9 (d), 130.5 (d), 136.7 (s); IR ($CCl_4$) 3590, 3080, 3040, 3000, 2880, 1600, 1500, 1380, 1340 cm$^{-1}$. Anal. Calcd for $C_{22}H_{31}NO_2$: C, 77.38; H, 9.15; N, 4.10. Found: C, 76.91; H, 8.91; N, 3.97.

**Reaction of Dioxetanes 1b,d with Morpholine. Dioxetane 1b.** From the reaction of dioxetane **1b** (154 mg, 0.834 mmol) and morpholine (80.0 mg, 0.888 mmol) in 7 mL of $CH_2Cl_2$ for 0.5 h were obtained after chromatography (3:1 methylene chloride/ethyl acetate as eluent) 13.3 mg (9%) ω-chloroacetophenone (**12b**) and 149 mg (65%) of **3b**; the latter was recrystallized from $CH_2Cl_2$ to yield colorless needles, mp 158–160 °C dec.

***N*-[(3-Chloro-2-hydroxy-2-phenylpropyl)oxy]morpholine (3b):** $^1$H NMR ($CDCl_3/CD_3OD$ = 10:1, 200 MHz) δ 3.30 (br s, 1 H, OH), 3.90–4.45 (m, 8 H, morpholine), AB pattern ($\delta_A$ = 4.42, $\delta_B$ = 4.98, $J$ = 12.2 Hz, 2 H, $CH_2OH$), AB pattern ($\delta_A$ = 4.65, $\delta_B$ = 4.72, $J$ = 10.2 Hz, 2 H, $CH_2Cl$), 7.30–7.50 (m, 3 H, arom H), 7.60 (m, 2 H, arom H); $^{13}$C NMR ($CD_3OD$, 50 MHz) δ 62.5 and 62.8 (t, $CH_2NCH_2$), 64.2 (t, $CH_2Cl$), 65.9 and 65.9 (t, $CH_2OCH_2$), 81.9 (t, $CH_2O$), 83.3 (s), 126.0 (d), 129.1 (d), 129.2 (d), 136.7 (s); IR (KBr) 3300–3200, 3030, 2980, 2900, 1510, 1460, 1400, 1370, 1330, 1310 cm$^{-1}$. Anal. Calcd for $C_{13}H_{18}ClNO_3$: C, 57.47; H, 6.68; N, 5.15. Found: C, 57.69; H, 6.74; N, 5.20.

**Dioxetane 1d.** From the reaction of dioxetane **1d** (108 mg, 0.450 mmol) and morpholine (43.0 mg, 0.477 mmol) in 7 mL of $CH_2Cl_2$ for 15 h were obtained after chromatography (10:1 methylene chloride/ethyl acetate as eluent) 11.1 mg (12%) of **12d** and 110 mg (74%) of **3d**; the latter colorless oil yielded after crystallization from petroleum ether (bp 30–50 °C)/$CH_2Cl_2$ colorless needles, mp 54–55 °C.

***N*-[(2-Benzyl-2-hydroxy-3-phenylpropyl)oxy]morpholine (3d):** $^1$H NMR ($CDCl_3$, 250 MHz) δ 2.69 (br t, $J$ = 10.8 Hz, 2 H, $CH_2NCH_2$), AB pattern ($\delta_A$ = 2.79, $\delta_B$ = 2.89, $J$ = 13.6 Hz, 4 H, $CH_2Ph$), 3.20 (br t, $J$ = 10.9 Hz, 2 H, $CH_2NCH_2$), 3.48 (s, 2 H, $CH_2O$), 3.54 (br t, $J$ = 10.9 Hz, 2 H, $CH_2OCH_2$), 3.88 (br s, 1 H, OH), 3.89 and 3.92 (br s, 2 H, $CH_2OCH_2$), 7.13–7.34 (m, 10 H, arom H); $^{13}$C NMR ($CDCl_3$, 63 MHz) δ 43.9 (t, $CH_2Ph$), 55.7 (t, $CH_2NCH_2$), 66.1 (t, $CH_2OCH_2$), 73.0 (t, $CH_2O$), 75.1 (s), 126.4 (d), 128.0 (d), 130.7 (d), 137.3 (s); IR ($CCl_4$) 3400, 3030, 2980, 2880, 1610, 1505, 1465, 1270, 1180, 1015 cm$^{-1}$. Anal. Calcd for $C_{20}H_{25}NO_3$: C, 73.37; H, 7.70; N, 4.28. Found: C, 73.79; H, 7.93; N, 4.31.

**Reaction of Dioxetanes 1a,d with Triethylamine.** Separate samples of ca. 0.5 mmol of dioxetanes **1a** and **1d** in 2 mL of $CH_2Cl_2$ were cooled to −20 °C, and equimolar amounts of triethylamine in 0.5 mL of $CH_2Cl_2$ were added. The dioxetanes were completely consumed within 5 min (negative KI test). The solvent and excess $Et_3N$ were evaporated at 20 °C/15 Torr to yield exclusively (by $^1$H NMR spectroscopy) quantitative amounts of the corresponding dioxetane cleavage products **12a** and **12d**. The same results were obtained when a catalytic amount of triethylamine (ca. 10 mol %) was used (30 min).

**Reaction of Dioxetane 1c with Tertiary Amines. Triethylamine.** A solution of dioxetane **1c** (57.0 mg, 0.249 mmol) in 2 mL of $CH_2Cl_2$ was cooled to −20 °C under argon gas, and triethylamine (27.0 mg, 0.267 mmol) in 1 mL of $CH_2Cl_2$ was added. After 30 min, the dioxetane had disappeared, and the solvent was evaporated at 20 °C/15 Torr to yield 79.0 mg (96%) of a pale yellow oil, which could not be further purified due to its thermal lability and hygroscopic nature. NMR spectroscopy of the crude product revealed exclusive formation of **4c**.

***N*-[(2,3-Epoxy-2-phenylpropyl)oxy]-*N*,*N*,*N*-triethylammonium bromide (4c):** $^1$H NMR ($CDCl_3$, 250 MHz) δ 1.30 (t, $J$ = 7.2 Hz, 9 H, $CH_3$), 2.81 (d, $J$ = 5.2 Hz, 1 H, epoxide H), 3.39 (d, $J$ = 5.2 Hz, epoxide H), 4.01 (q, $J$ = 7.2 Hz, 6 H, $NCH_2$), AB pattern ($\delta_A$ = 4.44, $\delta_B$ 5.30, $J$ = 10.3 Hz, 2 H, $CH_2ON$), 7.29–7.49 (m, 5 H, arom H); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 7.87 (q, $CH_3$), 53.8 (t, epoxide $CH_2$), 55.2 (t, $NCH_2$), 57.3 (s), 72.2 (t, $CH_2ON$), 125.7 (d), 128.1 (d), 128.4 (d), 135.5 (s).

**1,4-Diazabicyclo[2.2.2]octane (DABCO).** A solution of dioxetane **1c** (30.3 mg, 0.132 mmol) in 0.3 mL of $CDCl_3$ was placed into an NMR tube and cooled to −20 °C under argon gas, and a solution of DABCO (16.0 mg, 0.132 mmol) in 0.3 mL of $CDCl_3$ was added. The yellow color of the dioxetane disappeared instantaneously, and the solution was submitted to NMR analysis, which revealed total conversion of the dioxetane to yield exclusively the adduct **5c**.

***N*-[(2,3-Epoxy-2-phenylpropyl)oxy]-1,4-diazabicyclo[2.2.2]octyl bromide (5c):** $^1$H NMR ($CDCl_3$, 200 MHz) δ 2.82 (d, $J$ = 5.1 Hz, 1 H, epoxide H), 3.24 (d, $J$ = 5.1 Hz, 1 H, epoxide H), 3.45 (m, 6 H, $CH_2N$), 3.95 (m, 6 H, $CH_2NO$), AB pattern ($\delta_A$ = 4.68, $\delta_B$ = 5.42, $J$ = 10.9 Hz, 2 H, $CH_2ON$), 7.32–7.50 (m, 5 H, arom H); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 47.8 (t, $CH_2N$), 54.3 (t, epoxide $CH_2$), 55.6 (t, $CH_2NO$), 54.7 (s), 71.2 (t, $CH_2ON$), 126.0 (d), 128.4 (d), 128.7 (d), 135.5 (s).

**Reaction of Dioxetane 1c with Sulfur Nucleophiles. Thiophenol.** A solution of dioxetane **1c** (17.8 mg, 0.0778 mmol) in 0.3 mL of $CDCl_3$ was placed into an NMR tube and cooled to −20 °C under argon gas, and a solution of thiophenol (21.3 mg, 0.193 mmol) in 0.3 mL of $CDCl_3$ was added. After 10 min, the dioxetane was totally consumed (negative KI test), and by quantitative $^1$H NMR analysis (hexamethyldisiloxane as standard) there were detected the diol **11c** (78%) and the dioxetane cleavage product ω-bromoacetophenone (**12c**) (22%); the mass balance was 92%.

**3-Bromo-2-phenylpropane-1,2-diol[14] (11c):** $^1$H NMR (200 MHz, $CDCl_3$) δ 2.20 (br s, 1 H, OH), 3.50 (br s, 1 H, OH), AB pattern ($\delta_A$ = 3.82, $\delta_B$ = 3.93, $J$ = 10.7 Hz, 2 H, $CH_2Br$), 3.85 (br s, 2 H, $CH_2OH$), 7.30–7.45 (m, 5 H, arom H).

**Benzyl Mercaptan.** Following the above procedure, the reaction of dioxetane **1c** (33.4 mg, 0.146 mmol) and benzyl mercaptan (45.3 mg, 0.365 mmol) in 0.6 mL of $CDCl_3$ yielded after 10 min at −20 °C diol **10c** (>99%) and dioxetane cleavage product **12c** (<1%); the mass balance was 95%.

**Diphenyl Sulfide.** Following the above procedure, the reaction of dioxetane **1c** (26.9 mg, 0.117 mmol) and diphenyl sulfide (22.0 mg, 0.118 mmol) in 0.6 mL of $CDCl_3$ gave after 30 min at −20 °C the sulfonium salt **6c** (11%), epoxide **7c** (66%), epoxy alcohol **8c** (20%), and dioxetane cleavage product **12c** (3%); the mass balance was 86%. Additionally, ca. 5% of another, unidentified product with epoxide structure ($\delta$ 3.17 and 3.37, $J$ = 5.4 Hz) was detected. After 1 h at −20 °C, the signals of **6c** in the $^1H$ NMR spectrum had totally disappeared. Diphenyl sulfide was oxidized to diphenyl sulfoxide, which was identified by its $^{13}C$ NMR data.

***S*,*S*-Diphenyl-*S*-[(2,3-epoxy-2-phenylpropyl)oxy]sulfonium bromide (6c):** $^1H$ NMR ($CDCl_3$, 200 MHz, −20 °C) $\delta$ 2.79 (d, $J$ = 4.9 Hz, 1 H, epoxide H), 3.24 (d, $J$ = 4.9 Hz, 1 H, epoxide H), AB pattern ($\delta_A$ = 4.86, $\delta_B$ = 5.71, $J$ = 12.4 Hz, 2 H, $CH_2OS$); the aromatic signals were covered by the other products. Due to its lability, no satisfactory $^{13}C$ NMR spectrum nor elemental analysis could be obtained for **6c**.

**2-(Bromomethyl)-2-phenyloxirane[14] (7c):** $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 3.01 (d, $J$ = 5.2 Hz, 1 H, epoxide H), 3.20 (d, $J$ = 5.2 Hz, 1 H, epoxide H), AB pattern ($\delta_A$ = 3.65, $\delta_B$ = 3.92, $J$ = 11.1 Hz, 2 H, $CH_2Br$), 7.30–7.47 (m, 5 H, arom H).

**2,3-Epoxy-2-phenylpropan-1-ol[14] (8c):** $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 2.78 (d, $J$ = 5.3 Hz, 1 H, epoxide H), 2.86 (br s, 1 H, OH), 3.22 (d, $J$ = 5.3 Hz, 1 H, epoxide H), AB pattern ($\delta_A$ = 3.93, $\delta_B$ = 4.07, $J$ = 12.6 Hz, 2 H, $CH_2OH$), 7.24–7.40 (m, 5 H, arom H).

**Reactions of Dioxetanes 1c,d with Anionic Nucleophiles. General Procedure.** At 0 °C, cooled solutions of dioxetanes **1c,d** (ca. 0.1 M) in acetonitrile were added to 5–10 mL of a 1:1 acetonitrile/water mixture, which contained the corresponding potassium halide salt (10–100% excess). After total conversion of the dioxetane (negative KI test), the reaction mixture was diluted with 10–20 mL of water (in the case of KCN the solution was neutralized with 2 N HCl and extracted with methylene chloride (3 × 10 mL). The combined organic layers were dried with $MgSO_4$, and the solvent was removed at 20 °C/15 Torr. Product compositions of the crude mixtures were obtained by $^1H$ NMR spectroscopy (250 MHz) in $CDCl_3$; products were isolated by silica column chromatography.

**Reaction of Dioxetanes 1c,d with Potassium Cyanide. Dioxetane 1c.** Dioxetane **1c** (300 mg, 1.31 mmol) was treated with KCN (120 mg, 1.84 mmol) in 10 mL of a 10:1 acetonitrile/water mixture. The dioxetane was consumed instantaneously, and chromatography ($CH_2Cl_2$, followed by 20:1 $CH_2Cl_2$/methanol as eluent) afforded first 201 mg (60%) of carbonate **9c** as a colorless oil, which crystallized on treatment with *n*-pentane to give colorless needles, mp 63–65 °C. As a second fraction there was obtained 41.0 mg (17%) of epoxy alcohol **8c**.

**4-(Bromomethyl)-4-phenyl-2-oxo-1,3-dioxolane (9c):** $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ AB pattern ($\delta_A$ = 3.69, $\delta_B$ = 3.77, $J$ = 11.9 Hz, 2 H, $CH_2Br$), AB pattern ($\delta_A$ = 4.60, $\delta_B$ = 4.89, $J$ = 8.5 Hz, 2 H, $CH_2O$), 7.30–7.48 (m, 5 H, arom H); $^{13}C$ NMR ($CDCl_3$, 63 MHz) $\delta$ 38.3 (t, $CH_2Br$), 73.1 (t, $CH_2O$), 83.4 (s), 124.3 (d), 129.2 (d), 129.4 (d), 137.8 (s), 153.3 (s, C=O); IR ($CCl_4$) 3080, 2960, 1830, 1500, 1470, 1450, 1420, 1380, 1240, 1220, 1145 $cm^{-1}$. Anal. Calcd for $C_{10}H_9BrO_3$: C, 46.72; H, 3.53. Found: C, 46.46; H, 3.50.

**Dioxetane 1d.** Dioxetane **1d** (300 mg, 1.25 mmol) was treated with KCN (100 mg, 1.54 mmol) in 10 mL of a 10:1 acetonitrile/water mixture at 0 °C for 1 h. Chromatography (5:1 $CH_2Cl_2$/ethyl acetate as eluent) gave first 237 mg (71%) of carbonate **9d** as a colorless powder, which was recrystallized from petroleum ether (bp 30–50 °C)/$CH_2Cl_2$ to yield white cubes, mp 136–137 °C. As a second fraction there was obtained 54.0 mg (15%) of carbamic acid ester **9d'** as an oil, which crystallized on treatment with $CCl_4$ to give colorless needles, mp 107–109 °C.

**4,4-Dibenzyl-2-oxo-1,3-dioxolane (9d):** $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ AB pattern ($\delta_A$ = 2.94, $\delta_B$ = 3.16, $J$ = 14.4 Hz, 4 H, $CH_2Ph$), 4.18 (s, 2 H, $CH_2O$), 7.21–7.39 (m, 10 H, arom H); $^{13}C$ NMR ($CDCl_3$, 63 MHz) $\delta$ 43.9 (t, $CH_2Ph$), 69.8 (t, $CH_2O$), 84.4 (s), 127.6 (d), 128.7 (d), 130.4 (d), 133.5 (s), 154.0 (s, C=O); IR (KBr) 3070, 3040, 2930, 1790, 1720, 1495, 1240, 1200, 1170, 1060 $cm^{-1}$. Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.16; H, 6.02. Found: C, 76.12; H, 6.02.

**Carbamic acid 1,1-dibenzyl-2-hydroxyethyl ester (9d'):** $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ AB pattern ($\delta_A$ = 3.00, $\delta_B$ = 3.16, $J$ = 14.0 Hz, 4 H, $CH_2Ph$), 3.53 (d, $J$ = 6.5 Hz, 2 H, $CH_2O$), 3.87 (t, $J$ = 6.5 Hz, OH, exchanges with $D_2O$), 4.65 (br s, 2 H, $NH_2$, exchanges with $D_2O$), 7.18 (m, 10 H, arom H); $^{13}C$ NMR ($CDCl_3$, 63 MHz) $\delta$ 40.8 (t, $CH_2Ph$), 66.0 (t, $CH_2O$), 86.7 (s), 126.6 (d), 128.1 (d), 130.4 (d), 136.1 (s), 157.2 (s), C=O); IR (KBr) 3420, 3300, 3250, 3190, 2920, 1695, 1615, 1450, 1390, 1320 $cm^{-1}$. Anal. Calcd for $C_{17}H_{19}O_3$: C, 71.57; H, 6.71; N, 4.91. Found: C, 71.88; H, 6.94; N, 4.78.

**Reaction of Dioxetane 1c with Potassium Cyanide in Deuteriochloroform.** To a solution of dioxetane **1c** (27.8 mg, 0.121 mmol) in 0.6 mL of $CDCl_3$ was added solid potassium cyanide (8.00 mg, 0.123 mmol) at 0 °C. No conversion was observed by $^1H$ NMR monitoring after 30 min. Addition of about 10 mol % of 18-crown-6 caused total consumption of the dioxetane within 30 min ($^1H$ NMR monitoring). Besides unidentified products, mostly decomposition product **12c** and epoxy alcohol **8c** were observed (**12c**:**8c** = 68:31); the mass balance was ca. 75%.

**Reaction of Dioxetane 1c with Potassium Thiocyanate.** When dioxetane **1c** (300 mg, 1.31 mmol) in 3 mL of acetonitrile was slowly added to KSCN (285 mg, 2.66 mmol) in a 1:5 water/acetonitrile mixture (6 mL), the dioxetane was consumed instantaneously. Chromatography ($CH_2Cl_2$ followed by 3:1 $CH_2Cl_2$/MeOH as eluent) first afforded 185 mg (50%) of the cyclic sulfite **10c** as a colorless oil [dr = 55:45 (by $^1H$ NMR)], which crystallized in $CH_2Cl_2$/petroleum ether (bp 30–50 °C) to yield 73.0 mg of the major isomer as colorless needles, mp 70–72 °C. As a second fraction there was obtained 95.0 mg (36%) of epoxy alcohol **8c** and **11c** as a mixture [**8c**:**11c** = 37:63 (by $^1H$ NMR)].

**4-(Bromomethyl)-4-phenyl-1,3,2-dioxathiolane 2-Oxide (10c).** Minor isomer: $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ AB pattern ($\delta_A$ = 3.82, $\delta_B$ = 3.89, $J$ = 11.1 Hz, 2 H, $CH_2Br$), AB pattern ($\delta_A$ = 4.74, $\delta_B$ = 4.99, $J$ = 9.0 Hz, 2 H, $CH_2O$), 7.40 (m, 5 H, arom H); $^{13}C$ NMR ($CDCl_3$, 63 MHz) $\delta$ 37.4 (t, $CH_2Br$), 74.8 (t, $CH_2O$), 90.8 (s), 125.1 (d), 129.0 (d), 129.1 (d), 137.9 (s). Major isomer: $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 3.61 (s, 2 H, $CH_2Br$), AB pattern ($\delta_A$ = 4.73, $\delta_B$ = 4.84, $J$ = 9.1 Hz, 2 H, $CH_2O$), 7.40 (m, 5 H, arom H); $^{13}C$ NMR ($CDCl_3$, 63 MHz) $\delta$ 36.6 (t, $CH_2Br$), 73.8 (t, $CH_2O$), 91.2 (s), 125.6 (d), 128.7 (d), 128.8 (d), 137.2 (s); IR ($CCl_4$) 3400, 2940, 1440, 1220, 1040, 1025, 970, 900, 850, 700 $cm^{-1}$. Anal. Calcd for $C_9H_9BrO_3S$: C, 39.01; H, 3.27. Found: C, 39.24; H, 3.25.

**Reaction of Dioxetanes 1c,d with Potassium Bromide. Dioxetane 1c.** Dioxetane **1c** (222 mg, 0.969 mmol) reacted with KBr (130 mg, 1.03 mmol) in 8 mL of acetonitrile and 0.8 mL of water within 0.5 h. After workup there was obtained 143 mg (92%) of a colorless oil, which contained epoxy alcohol **8c**, diol **11c**, and epoxide **7c** (**8c**:**11c**:**7c** = 79:11:10).

**Dioxetane 1d.** Dioxetane **1d** (263 mg, 1.09 mmol) and KBr (300 mg, 2.50 mmol) in 10 mL of acetonitrile and 0.5 mL of water gave, within 6 h, 233 mg (88%) of crude product, which contained diol **11d** and dioxetane cleavage product **12d** in a ratio of 89:11. Chromatography (4:1 $CH_2Cl_2$/ethyl acetate as eluent) afforded 178 mg (68%) of diol **11d** as an oil, which crystallized on treatment with petroleum ether (bp 30–50 °C). Recrystallization from $CH_2Cl_2$/petroleum ether gave colorless plates, mp 93–95 °C.

**2-Benzyl-3-phenylpropane-1,2-diol (11d):** $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 1.85 (br s, 2 H, OH) AB pattern ($\delta_A$ = 2.73, $\delta_B$ = 2.82, $J$ = 13.6 Hz, 4 H, $CH_2Ph$), 3.80 (s, 2 H, $CH_2O$), 7.12–7.28 (m, 10 H, arom H); $^{13}C$ NMR ($CDCl_3$, 63 MHz) $\delta$ 43.3 (t, $CH_2Ph$), 66.3 (t, $CH_2O$), 74.4 (s), 126.6 (d), 128.3 (d), 130.6 (d), 136.7 (s); IR ($CCl_4$) 3380, 3020, 2970, 2900, 1480, 1440, 1400, 1300, 1230, 1090 $cm^{-1}$. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.48; H, 7.47.

**Reaction of Dioxetane 1c with Potassium Bromide in Deuteriochloroform.** To a solution of dioxetane **1c** (25.7 mg, 0.112 mmol) in 0.6 mL of $CDCl_3$ was added solid potassium bromide (13.4 mg, 0.113 mmol). After 30 min (no conversion was observed by $^1H$ NMR monitoring), ca. 10 mol % of 18-crown-6 was added. The dioxetane was completely consumed within 30 min to afford cleavage product **12c** and epoxy alcohol **8c**, besides unidentified products (**8c**:**12c** = 30:70); the mass balance was ca. 80%.

**Reaction of Dioxetanes 1c,d with Potassium Chloride. Dioxetane 1c.** A sample of 90.0 mg (0.393 mmol) of dioxetane **1c** was treated with 55.0 mg (0.738 mmol) of potassium chloride in a mixture of 4 mL of acetonitrile and 0.5 mL of water. Within 24 h all dioxetane was consumed (monitored by TLC) to yield 75.5 mg (92%) of a mixture of epoxy alcohol **8c**, diol **11c**, and epoxide **7c** (**8c**:**11c**:**7c** = 27:70:3).

**Dioxetane 1d.** On treatment of a sample of 95.3 mg (0.397 mmol) of dioxetane **1d** with 60.0 mg (0.805 mmol) of potassium chloride in a mixture of 4 mL of acetonitrile and 0.5 mL of water for 96 h, 85.3 mg (90%) of dioxetane **1d** was recovered after the usual workup.

**Reaction of Dioxetane 1c with Potassium Hydroxide.** A solution of dioxetane **1c** (100 mg, 0.436 mmol) in 10 mL of methanol was cooled to −10 °C, and a solution of KOH (76.0 mg, 1.36 mmol) in MeOH was added to it. After 1 h, the dioxetane was completely consumed (negative KI test), and the mixture was neutralized with 2 N HCl. The methanol was evaporated at 20 °C/15 Torr, and the residue was diluted with 20 mL of water and extracted with methylene chloride (3 × 10 mL). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ (1 × 10 mL) and dried over $MgSO_4$, and the solvent was evaporated at 20 °C/15 Torr to yield 60.0 mg (92%) of epoxy alcohol **8c** as the only product (by $^1H$ NMR).

**Reaction of Dioxetane 1c with Potassium Superoxide.** A sample of 105 mg (0.458 mmol) of dioxetane **1c** in 3 mL of dry acetonitrile was added to a suspension of 50.0 mg (0.703 mmol) of potassium superoxide in 5 mL of dry acetonitrile, which contained ca. 10 mol % of 18-crown-6. After 15 min, the dioxetane had disappeared (negative KI test), and 5 mL of water was added. Extraction with $CH_2Cl_2$ was followed by drying over $MgSO_4$ and evaporation of the solvent at 20 °C/15 Torr to yield 64.3 mg (93%) of epoxy alcohol **8c** as the only product (by $^1H$ NMR).

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**Registry No.** **1a**, 35322-45-3; **1b**, 136749-73-0; **1c**, 136132-07-5; **1d**, 40814-69-5; **2b**, 141248-81-9; **2c**, 141248-82-0; **2d**, 141248-83-1; **3b**, 141248-84-2; **3d**, 141248-85-3; **4c**, 141248-86-4; **5c**, 141248-87-5; **6c**, 141248-88-6; **7c**, 64398-73-8; **8c**, 141248-89-7; **9c**, 141248-90-0; **9d**, 141248-91-1; **9d'**, 141248-92-2; **10c**, 141248-93-3; **11c**, 141248-94-4; **11d**, 92527-70-3; **12a**, 98-86-2; **12b**, 532-27-4; **12c**, 70-11-1; **12d**, 102-04-5; DABCO, 280-57-9; $(i\text{-}Pr)_2NH$, 75-31-0; $CN^-$, 57-12-5; $Br^-$, 24959-67-9; $Cl^-$, 16887-00-6; $NET_3$, 121-44-8; PhSH, 108-98-5; $PhCH_2SH$, 100-53-8; $Ph_2S$, 139-66-2; $SCN^-$, 302-04-5; $OH^-$, 14280-30-9; $O_2^{\bullet-}$, 11062-77-4; morpholine, 110-91-8.

# Homolytic and Heterolytic Cleavage Energies for Carbon–Nitrogen Bonds

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**Abstract:** Using calorimetric and electrochemical techniques described in previous reports, we have determined the heterolytic and homolytic bond energies at 25 °C in sulfolane for the carbon–nitrogen bonds in the compounds produced by reactions of nine resonance-stabilized carbenium ions with nitranions formed by deprotonating the following nitrogen acids: succinimide, phthalimide, carbazole, and 3,6-dibromocarbazole.

## Introduction

In a series of recent publications,[1-6] we have reported heterolytic bond energies ($\Delta H_{het}$'s) derived from the calorimetric heats of reaction of resonance-stabilized carbenium ions with various types of anions and neutral compounds at 25 °C in tetramethylene sulfone (sulfolane), a highly polar solvent with unusual resistance to attack by both acids and bases. Heats of heterolysis ($\Delta H_{het}$'s) were obtained directly from the heats of reaction of the carbenium ions and anions simply by changing the sign, and over 200 values have been obtained for carbon–carbon, carbon–oxygen, and carbon–sulfur bonds. Most of the $\Delta H_{het}$'s obtained in this way were converted into homolytic bond energies ($\Delta H_{homo}$'s) through the use of the thermodynamic cycle shown in Scheme I.

The free energy of electron transfer ($\Delta G_{ET}$), which relates $\Delta H_{homo}$ to $\Delta H_{het}$, is derived from the oxidation potential of the anion and the reduction potential of the carbenium ion. In turn, these important values have been obtained in our laboratory by several voltammetric techniques: ordinary cyclic voltammetry, second-harmonic ac voltammetry, and Osteryoung square-wave voltammetry (OSWV).[5] In view of the instability of the radicals derived by oxidation and reduction of the anions and carbenium ions, much effort was employed in obtaining reversible redox potentials by the methods listed above. In general, there was remarkably good agreement between results obtained by the three methods, even though in some cases the redox potentials were irreversible by one or another of the techniques. However, in the present study involving carbenium ions and nitranions, we have used only CV and SHACV for all our electrochemical measurements.

**Scheme I.** Thermodynamic Cycle Relating Homolytic and Heterolytic Bond Energies to Electron-Transfer Energies

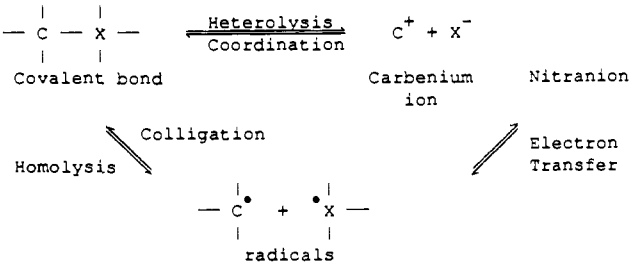
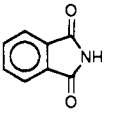
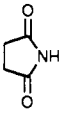
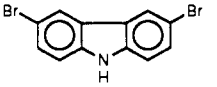
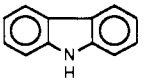



**Table I.** Structures of Nitranion Precursors

| compound | structure |
|---|---|
| phthalimide |  |
| succinimide |  |
| 3,6-dibromocarbazole |  |
| carbazole |  |

The second important concern in combining calorimetric enthalpies with electrode potentials is that the latter properties are free energy terms. In some of our earlier work,[2,5] we demonstrated that entropies of electron transfer for a number of compounds were remarkably small so that enthalpies and free energies of electron transfer could be used almost interchangeably. The entropies of

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