1,3-Dioxolane Formation by Nucleophilic Attack of Diazoalkanes on the Peroxide Bond of 1,2-Dioxetanes

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The reaction of the 1,2-dioxetanes **1a–d** with the diazoalkanes **2**α–η was investigated. The two 3,3-disubstituted (3,3-dimethyl- and 3-(bromomethyl)-3-phenyl) dioxetanes (**1a** and **1b**), trimethyldioxetane (**1c**), and tetramethyldioxetane (**1d**) gave with the various diazoalkanes **2** the corresponding 1,3-dioxolanes **3** (insertion products) and/or the dioxetane-derived ketones **4** (fragmentation). Nucleophilic attack by the negatively charged carbon pole of the diazoalkane on the sterically less hindered site of the dioxetane peroxide bond affords the 1,3-dioxolane **3** after cyclization with denitrogenation of the resulting O,N dipole. The O,C dipole, formed by the nucleophilic attack of the negatively charged nitrogen pole on the dioxetane, is proposed as precursor to the ketones **4** through Grob-type fragmentation with regeneration of the diazoalkane.

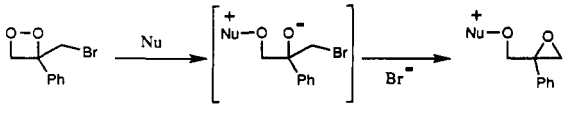
Introduction

Well-established examples of S_N1-type reactions of peroxides constitute the alkylation of hydrogen peroxide and alkyl hydroperoxides[1] by diazoalkanes to form the corresponding alkyl hydroperoxides and dialkyl peroxides. The mechanism entails proton transfer of the peroxide to the diazoalkane, loss of molecular nitrogen, and subsequent coupling of the carbenium ion with the peroxide anion.

Less well understood is the mechanism of dibenzoyl peroxides with diazoalkanes. For example, bis(4-nitrobenzoyl) peroxide leads on treatment with an excess of diazomethane to methyl 4-nitrobenzoate, for which nucleophilic attack of the diazo carbon at the carbonyl group of the diacyl peroxide has been proposed.[2] For the reaction of 4-substituted dibenzoyl peroxides with diazoalkanes, besides radical reactions, S_N2 attack on the peroxide bond has also been documented.[3] Such a pathway would account for bis(benzoyloxy)diphenylmethane formation in the reaction of dibenzoyl peroxide and diphenyldiazomethane.[4]

Peracids convert diphenyldiazomethane[5] and cyclic α-diazo ketones[6] into the corresponding benzophenones and 1,2-diketones, with the carboxylic acid as the peracid-derived product. Nucleophilic attack of the diazo carbon on the hydrogen-bearing peroxy oxygen atom was postulated as the initial step, followed by loss of molecular nitrogen and proton transfer to the carboxylate anion.

Recently, we have demonstrated that 3,3-disubstituted 1,2-dioxetanes form stable adducts with carbanions[7] and heteroatom nucleophiles[8] through an S_N2-type reaction. For example, 3-(bromomethyl)-3-phenyldioxetane was shown to undergo nucleophilic attack at the sterically less hindered site of the dioxetane, and intramolecular bromide elimination led subsequently to epoxide formation.

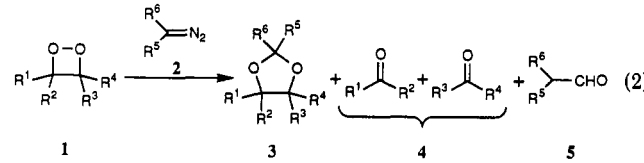


(1)

The reaction of diazoalkanes with dioxetanes had not been previously investigated, and it was of mechanistic interest to assess whether these dipolar species undergo S_N2-type reaction with such strained peroxides. Nucleophilic attack of the negatively charged diazo carbon atom at the sterically exposed oxygen atom of the dioxetane ring should lead to a dipolar adduct, which would be expected to form 1,3-dioxolanes on elimination of N_2 and subsequent cyclization. That this is a prominent pathway is revealed in Scheme 1. Herein we present the detailed results of this study.

Results

The transformations of dioxetanes **1a–d** with the diazoalkanes **2**α–η were carried out at low temperatures (−40 to 0 °C) under a nitrogen gas atmosphere. The



(2)

1 3 4 5

resulting 1,3-dioxolanes **3** were isolated and purified by column chromatography and fully characterized. The dioxetane fragmentation products **4** were also obtained. Formaldehyde, which resulted from fragmentation of dioxetane **1a**, transformed the diazoalkanes **2** to the aldehydes **5**. This was confirmed by treating diazoalkane **2**δ with an excess of gaseous formaldehyde in chloroform, which gave diphenylacetaldehyde (**5a**δ) in 91% yield.

The results of the product studies for the reactions of the dioxetanes **1** with diazoalkanes **2** are summarized in Table 1. Alkyl- and aryl-substituted diazoalkanes **2**α–δ gave with dioxetane **1a** in methylene chloride at 0 °C the corresponding 1,3-dioxolanes **3** in good yields (58–75%). In addition, 25–42% of the dioxetane cleavage product acetone was detected in the crude product mixture by ^{1}H NMR spectroscopy (Table 1, entries 1–4). The resonance-

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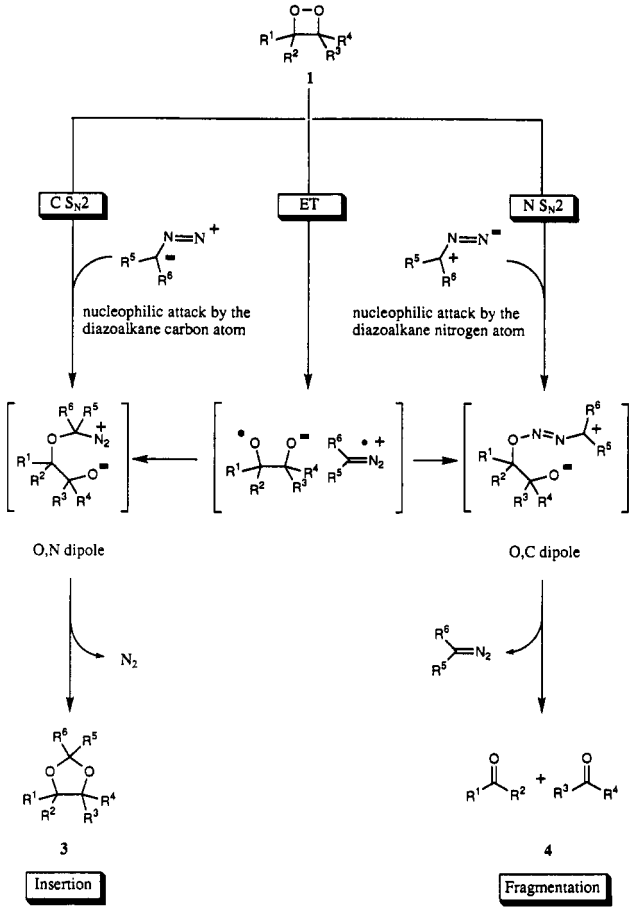
Scheme 1. Possible Mechanistic Pathways for the Reaction of Dioxetanes 1 with Diazoalkanes 2



stabilized diazoalkanes methyl diazomalonate (2ϵ), 2-diazo-1-phenylbutane-1,3-dione (2ϕ), and 1-diazo-3,5-dimethylcyclohexa-2,5-dien-4-one (2η) resulted in the slow decomposition of dioxetane **1a** by fragmentation. A control experiment under identical conditions showed that in the absence of diazoalkane 2δ the dioxetane **1a** decomposed to less than 10%.

To rule out carbene insertion for the formation of the 1,3-dioxolanes **3**, dioxetane **1a** was allowed to react with diazoalkane 2δ under irradiation with a sodium vapor lamp at 0 and −40 °C in deuteriochloroform. The amount of 1,3-dioxolane decreased from 58% (without irradiation, Table 1, entry 4) to 24% at 0 °C and 9% at −40 °C (with irradiation; Table 1, entries 5 and 6). The remaining diphenyldiazomethane (2δ) was converted into the corresponding azine.

Dioxetane **1b** afforded with diazoalkane 2δ at −40 °C in methylene chloride 85% of 1,3-dioxolane (**3b**δ). Additionally, 8% of 2-(bromomethyl)-2-phenyloxirane (**6b**) and 7% of benzophenone were detected in the crude product mixture by ^{1}H NMR spectroscopy, but no dioxetane cleavage product was found. An attempted trapping experiment in a 1:1 mixture of methanol/methylene chloride resulted only in 66% of 1,3-dioxolane (**3b**δ), 18% of epoxide **6b**, and 16% of benzophenone (Table 1, entries 7 and 8), but no methanol adducts.

Trimethyldioxetane (**1c**) and diazoalkane 2δ at 0 °C gave within 240 h 5% of 4,4,5-trimethyl-2,2-diphenyl-1,3-dioxolane (**3c**δ) and 95% of dioxetane cleavage products (Table 1, entry 9). Tetramethyldioxetane (**1d**) slowly decomposed within ca. 400 h when treated with diazoalkane 2δ at 0 °C in deuteriochloroform; no 1,3-dioxolane could be observed (Table 1, entry 10).

Discussion

The formation of 1,3-dioxolanes **3** can formally be regarded as insertion of a carbene unit into the peroxide bond of the dioxetane. However, direct carbene insertion can be excluded since reaction of dioxetane **1a** with diazoalkane 2δ in the presence of light did not result in an enhanced yield of 1,3-dioxolane **3a**δ.

Other possible mechanistic pathways are shown in Scheme 1. Nucleophilic attack of the negatively charged diazoalkane carbon atom (pathway C S_N2) at the sterically less hindered site of the 3,3-disubstituted dioxetane would lead to the O,N dipole (Scheme 1), which on loss of molecular nitrogen and cyclization would afford the 1,3-dioxolanes **3**. Electron transfer (pathway ET) from the diazoalkane **2** to the dioxetane **1** would lead to a radical pair, which on recombination would generate the O,N or O,C dipoles. The latter could also arise from direct nucleophilic attack of the negatively charged diazoalkane nitrogen atom (pathway N S_N2) on the dioxetane and could, in principle, fragment into the carbonyl compounds **4** with regeneration of the diazoalkane.

The chemistry of radical cations of diazoalkanes is well investigated.[9] The electrochemically generated radical cation 2$\delta^{\bullet+}$ undergoes a radical chain reaction to form tetraphenylethylene and, in the presence of water, benzophenone and benzpinacolone. On the other hand, radical anions of α-bromo ketones are known to eliminate bromide and form dehalogenated products.[10] Hence, should electron transfer play a significant role in this process, the radical anion of dioxetane **1b** would be expected to fragment into formaldehyde and the bromoacetophenone radical anion. Loss of the bromide ion and hydrogen atom abstraction should lead to acetophenone, i.e., the debrominated fragmentation product. None of the expected products mentioned above could be detected in the reaction of dioxetanes **1** with diazoalkanes **2**, which makes electron transfer an unlikely pathway for the formation of 1,3-dioxolanes **3**. In fact, previous work has convincingly demonstrated that even for effective electron donors such as lithium triphenylmethide[7] and dihydronicotinamides[11] S_N2 reactivity prevails for the bromo-substituted dioxetane **1b**.

Nucleophilic attack of the negatively charged diazoalkane carbon atom (pathway C S_N2, Scheme 1) at the sterically less hindered site of the dioxetane is proposed to lead to the O,N-centered 1,7 dipole, which may cyclize by subsequent intramolecular S_N1 or S_N2 reaction to the 1,3-dioxolanes **3**. Since nucleophilic substitutions are sensitive to steric factors, the ease of nucleophilic attack on the peroxide bond of the dioxetane should be reflected in the rate of product formation. Indeed, 3,3-dimethyldioxetane (**1a**) reacts significantly faster with diazoalkane 2δ than trimethyldioxetane (**1c**), while tetramethyldioxetane (**1d**) does not form any 1,3-dioxolane at all; instead, slow fragmentation into the carbonyl products **4** is observed with diazoalkane 2δ.

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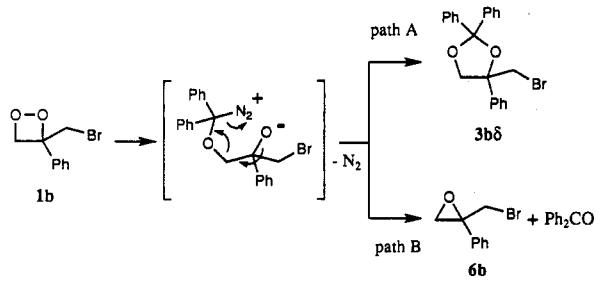
Table 1. Product Studies of the Reaction of Dioxetanes 1 with Diazoalkanes 2

	dioxetane				diazoalkane						products[a,b] (%)	
entry		R^1	R^2	R^3	R^4		R^5	R^6	solvent	time (h)	convn[b,c] (%)	mb[b,d] (%)	insertion[e] 3	fragmentation 4
1	1a	Me	Me	H	H	2α	H	H	Et_2O	22[f]	100[g]	68	*h* (71)	*h*
2	1a	Me	Me	H	H	2β	Ph	H	CH_2Cl_2	12	100[g]	90	74 (48)	26[i]
3	1a	Me	Me	H	H	2γ	Ph	Me	CH_2Cl_2	12	100[g]	80	75 (50)	25[i]
4	1a	Me	Me	H	H	2δ	Ph	Ph	CH_2Cl_2	14	100[g]	>95	58 (39)	42[i]
5	1a	Me	Me	H	H	2δ	Ph	Ph	$CDCl_3$[k]	14	>95	>95	24	76[l]
6	1a	Me	Me	H	H	2δ	Ph	Ph	$CDCl_3$[k]	14[m]	>95	>95	9	91[n]
7	1b	Ph	CH_2Br	H	H	2δ	Ph	Ph	CH_2Cl_2	3.5[m]	100[g]	>95	85 (82)[o]	<5
8	1b	Ph	CH_2Br	H	H	2δ	Ph	Ph	CH_2Cl_2/MeOH (1:1)	3.5[m]	100[g]	>95	66 (62)[p]	<5
9	1c	Me	Me	Me	H	2δ	Ph	Ph	CH_2Cl_2	240	100[g]	84	4 (1)	96
10	1d	Me	Me	Me	Me	2δ	Ph	Ph	$CDCl_3$	400	100[g]	>95	<5	>95

[a] Product distribution calculated from the ^1H NMR spectrum of the crude product mixture by using hexamethyldisiloxane as internal standard. [b] 5% error of stated value. [c] Conversion calculated from the ^1H NMR spectrum of the crude product mixture by using hexamethyldisiloxane as internal standard. [d] Mass balance calculated from the ^1H NMR spectrum of the crude product mixture by using hexamethyldisiloxane as internal standard. [e] Isolated yields in brackets. [f] At −20°C. [g] Negative peroxide test (KI/HOAc). [h] Not determined. [i] Includes aldehydes 5 as secondary products of CH_2O from fragmentation of dioxetane 1a and diazoalkanes 2. [k] Irradiation with two 150-W sodium vapor lamps. [l] Additionally, 31% of diphenylacetaldehyde 5aδ and 22% of tetraphenylazine were observed in the ^1H NMR spectrum of the crude product mixture by using hexamethyldisiloxane as internal standard. [m] At −40 °C. [n] Additionally, 26% of diphenylacetaldehyde 5aδ and 32% of tetraphenylazine were observed in the ^1H NMR spectrum of the crude product mixture by using hexamethyldisiloxane as internal standard. [o] Additionally, 2-(bromomethyl)-2-phenyloxirane (**6b**) (8%) and benzophenone (7%) were observed. [p] Additionally, 2-(bromomethyl)-2-phenyloxirane (**6b**) (18%) and benzophenone (16%) were observed.

Scheme 2. Mechanism of 1,3-Dioxolane 3bδ and Epoxide 6b Formation in the Reaction of Dioxetane 3b with Diazoalkane 2δ



1,3-Dioxolanes should be favored for diazoalkanes with the negatively charged pole localized at the carbon atom of the diazo group, while resonance stabilization of the negative charge should decrease the rate of 1,3-dioxolane formation. As can be seen from Table 1 (entries 1–4), for the alkyl- and aryl-substituted diazoalkanes 2α–δ the 1,3-dioxolanes **3** were produced efficiently, while for the resonance-stabilized diazoalkanes 2ε–η no 1,3-dioxolanes were observed. For the latter, again slow fragmentation into ketone products prevailed. This lack of reactivity is also reported for the reaction of diazoacetic ester and vinyldiazomethane with alkyl hydroperoxides.[12]

In contrast to the dioxetanes **1a** and **1c**, 3-(bromomethyl)-3-phenyldioxetane (**1b**) additionally forms equal amounts of the corresponding epoxide **6b** and benzophenone with diphenyldiazomethane (2δ). This can be explained by primary nucleophilic attack of the diazoalkane 2δ on the peroxide bond of the dioxetane **1b** and either elimination of molecular nitrogen to form 1,3-dioxolane **3bδ** (path A, Scheme 2) or back-side attack at the former C-4 atom of the dioxetane ring with elimination of benzophenone and molecular nitrogen (path B, Scheme 2).

Attempts to trap the postulated dipolar intermediate with methanol only resulted in a minor change in the product distribution (Table 1, entries 7 and 8). Presumably, the protic methanol solvates the charges of the dipole more effectively so that rotations become more feasible and the required conformation for the S_N2 displacement more probable. Be this as it may, the occurrence of epoxide **6b** and benzophenone support the nucleophilic reaction pathway proposed in Schemes 1 and 2. Recently, such epoxide formation and Grob-type fragmentations have been documented for numerous nucleophiles.[13]

Besides 1,3-dioxolane formation, some dioxetane cleavage products were observed in all reactions except for dioxetane **1b**. In fact, as already stated, for the resonance-stabilized diazoalkanes 2ε–η dioxetane fragmentation into carbonyl products **4** was the only observed process. Control experiments showed that dioxetane decomposition is accelerated in the presence of diazoalkanes **2**, which implies the direct involvement of these 1,3 dipoles in the fragmentation process.

We suggest nucleophilic attack of the diazoalkane nitrogen atom (pathway N S_N2, Scheme 1) to form the O,C-centered 1,7 dipole, which fragments into the dioxetane cleavage products **4**. Thus, the product ratio of 1,3-dioxolanes **3** (insertion) *versus* carbonyl products **4** (fragmentation) reflects competitive nucleophilic attack by the diazoalkane carbon and nitrogen atoms, i.e., the pathways C S_N2 versus N S_N2 in Scheme 1. The alkyl- and aryl-substituted diazoalkanes 2α–δ predominantly form 1,3-dioxolanes through nucleophilic attack by the diazoalkane carbon atom, while the resonance-stabilized diazoalkanes 2ε–η promote fragmentation of the dioxetanes through nucleophilic attack by the diazoalkane nitrogen atom. The possibility of Grob-type fragmentation of the O,N dipole (pathway C S_N2, Scheme 1) cannot be disposed, but to propose that only this intermediate intervenes does not account for all the experimental facts presented herein, especially that for the resonance-stabilized diazoalkanes 2ε–η no insertion products **3** and only fragmentation ketones **4** were observed.

To summarize, dioxetanes **1** undergo nucleophilic substitution with diazoalkanes **2** at the peroxide bond. The 1,3-dioxolane **3** insertion products are formed through pathway C S_N2, while the dioxetane cleavage products **4**

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(13) (a) Adam, W.; Andler, S.; Heil, M. *Angew. Chem.* **1991**, *103*, 1395. (b) Adam, W.; Heil, M.; Voerckel, V. *J. Org. Chem.* **1992**, *57*, 2680; see also refs 7 and 8.

derive from the competitive pathway N S_N2 in Scheme 1. Electron-transfer processes do not appear to play a significant role in the reaction of dioxetanes with diazoalkanes.

Experimental Section

General Aspects. Melting points were taken on a Reichert Thermovar Kofler apparatus and are uncorrected. ^1H NMR spectra: Bruker AC 200 (200 MHz) and Bruker AC 250 (250 MHz), TMS as internal standard. ^{13}C NMR spectra: Bruker AC 200 (50 MHz) and Bruker AC 250 (63 MHz), $CDCl_3$ as internal standard. Infrared spectra: Perkin-Elmer 1420 ratio recording infrared spectrophotometer. Mass spectra: Finnigan MAT 8200 and Finnigan MAT 90. Combustion analyses were carried out by the Microanalytical Division of the Institute of Inorganic Chemistry, University of Würzburg. Column chromatography: silica gel (63–200 μm) from Woelm with an absorbant/substrate ratio of ca. 100:1. Thin-layer chromatography (TLC): Polygram SIL G/UV_{254} (40 × 80 mm) from Machery and Nagel. Peroxides were detected with 10% aqueous KI solution, other compounds with a 5% ethanolic solution of molybdophosphoric acid or iodine vapor. Dioxetanes **1a–d** were synthesized by known literature methods.[13a,14]

The product data in the individual experiments represent absolute *isolated yields*, while in Table 1 (for mechanistic convenience) the relative yields (normalized to 100%) of the insertion product **3** and the fragmentation products **4** (includes aldehyde **5**; cf. footnote *i* in Table 1), as determined by NMR analysis directly on the crude product mixture before workup; all other side products have been ignored in Table 1.

Caution! β-Bromo hydroperoxides and 3,3-disubstituted 1,2-dioxetanes **1a,b** may decompose spontaneously when allowed to warm over 0 °C. Especially dioxetane **1a** must be handled with extreme care, since it detonates at even lower temperatures.

General Procedure for the Reaction of Dioxetane 1a with Diazoalkanes 2. Dioxetane **1a** (2.20–3.40 mmol) in 25 mL of methylene chloride [for diazomethane (**2α**), ether was necessary] was cooled to 0 or −40 °C under a nitrogen gas atmosphere, and equimolar amounts of diazoalkane **2** in 5 mL of methylene chloride were added. Stirring at 0 °C was continued until a negative peroxide test (KI/HOAc) indicated complete conversion of the dioxetane. The solvent was evaporated at 20 °C/15 Torr in the presence of catalytic amounts (ca. 10 mol %) of silica gel to convert the remaining diazoalkane into the corresponding azine. The product mixture was purified by column chromatography on silica gel.

Diazomethane (2α).[15] According to the general procedure, 300 mg (3.40 mmol) of dioxetane **1a** was taken up in 25 mL of ether, which contained 143 mg (3.40 mmol) of diazoalkane **2α** and stirred for 22 h at −20 °C. Workup and silica gel chromatography by eluting with a 1:1 mixture of methylene chloride/petroleum ether (30–50 °C) afforded 4,4-dimethyl-1,3-dioxolane (**3aα**) in 71% yield. ^1H and ^{13}C NMR spectra were in accordance with literature data.[16]

Phenyldiazomethane (2β).[17] According to the general procedure, 300 mg (3.40 mmol) of dioxetane **1a** and 402 mg (3.40 mmol) of diazoalkane **2β** in 25 mL of methylene chloride were stirred for 12 h at 0 °C. Workup and silica gel chromatography by eluting with a 1:1 mixture of methylene chloride/petroleum ether (30–50 °C) afforded as the first fraction 72.0 mg (10%) of 1,4-diphenylazine, as the second fraction 336 mg (48%) of 4,4-dimethyl-2-phenyl-1,3-dioxolane (**3aβ**), and as the third fraction 49.0 mg (12%) of phenylacetaldehyde (**5aβ**). ^1H and ^{13}C NMR data of 1,4-diphenylazine and aldehyde **5aβ** were identical to those of authentic samples, and the spectral data of dioxolane **3a** were in accordance with literature data.[18]

1-Diazo-1-phenylethane (2γ).[17] According to the general procedure, 200 mg (2.27 mmol) of dioxetane **1a** and 300 mg (2.27 mmol) of diazoalkane **2γ** were stirred in 25 mL of methylene chloride at 0 °C for 12 h. Workup and silica gel chromatography by eluting with a 1:1 mixture of methylene chloride/petroleum ether (30–50 °C) afforded as the first fraction 53.0 mg (10%) of 1,4-dimethyl-1,4-diphenylazine and as the second fraction 251 mg (50%) of 2,4,4-trimethyl-2-phenyl-1,3-dioxolane (**3aγ**) as a colorless oil. The third fraction contained 45.0 mg (9%) of phenylpropionaldehyde (**5aγ**). The azine and aldehyde **5aγ** were identified by comparison of their ^1H and ^{13}C NMR data with those of authentic samples.

2,4,4-Trimethyl-2-phenyl-1,3-dioxolane (3aγ): TLC [1:1 methylene chloride/petroleum ether (30–50 °C)], R_f = 0.39; IR (CCl_4) 3050, 3010, 2960, 2920, 2850, 1720, 1480, 1450, 1420, 1375, 1365, 1235, 1200, 1175, 1105, 1075, 1060, 1045, 1020, 975, 925, 880 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.69 (s, 3H, CH_3), AB pattern (δ_A = 3.54, δ_B = 3.84, J = 8.1 Hz, 2H), 7.31–7.58 (m, 5H, arom H); ^{13}C NMR ($CDCl_3$) δ 25.8 (q, CH_3), 27.8 (q, CH_3), 29.7 (q, CH_3), 75.3 (t, C-5), 79.7 (s, C-4), 109.3 (s, C-2), 125.2 (d), 127.5 (d), 127.9 (d), 144.9 (s). Anal. Calcd for $C_{12}H_{16}O_2$ (192.3): C, 74.95; H, 8.40. Found: C, 75.06; H, 8.51.

Diphenyldiazomethane (2δ).[19] According to the general procedure, 200 mg (2.27 mmol) of dioxetane **1a** was allowed to react with 441 mg (2.27 mmol) of diazoalkane **2δ** in 25 mL of methylene chloride for 14 h at 0 °C. Workup and silica gel chromatography by eluting with a 1:2 mixture of methylene chloride/petroleum ether (30–50 °C) afforded as the first fraction 83.0 mg (13%) of tetraphenylazine, as the second fraction 250 mg (39%) of 4,4-dimethyl-2,2-diphenyl-1,3-dioxolane (**3aδ**), and as the third fraction 122 mg (19%) of diphenylacetaldehyde (**5aδ**). Tetraphenylazine and aldehyde **5aδ** were identified by comparison of their ^1H and ^{13}C NMR data with those of authentic samples.

4,4-Dimethyl-2,2-diphenyl-1,3-dioxolane (3aδ): mp 83–84 °C; TLC [1:2 methylene chloride/petroleum ether (30–50 °C)], R_f = 0.37; IR (CCl_4) 3040, 3010, 2930, 1510, 1454, 1385, 1360, 1340, 1225, 1210, 1190, 1135, 1080, 1065 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43 (s, 6H, CH_3), 3.47 (s, 2H, CH_2O), 7.34–7.50 (m, 10H, arom H); ^{13}C NMR ($CDCl_3$) δ 27.1 (q, CH_3), 76.1 (t, C-5), 80.3 (s, C-4), 110.0 (s, C-2), 126.5 (d), 127.7 (d), 128.1 (d), 144.1 (s). Anal. Calcd for $C_{17}H_{18}O_2$ (254.4): C, 80.27; H, 7.17. Found: C, 80.62; H, 7.36.

Methyl Diazomalonate (2ε).[20] According to the general procedure, 20.0 mg (0.227 mmol) of dioxetane **1a** and 35.9 mg (0.227 mmol) of diazoalkane **2ε** in 0.8 mL of deuteriochloroform were allowed to stir for 157 h at 0 °C. After this time 47% of the dioxetane was consumed as monitored by ^1H NMR spectroscopy, and acetone was the only product.

2-Diazo-1-phenylbutane-1,3-dione (2θ).[20] According to the general procedure, 20.0 mg (0.227 mmol) of dioxetane **1a** and 42.7 mg (0.227 mmol) of diazoalkane **2θ** were dissolved in 0.8 mL of deuteriochloroform and allowed to stir at 0 °C for 81 h. After this time the dioxetane was completely consumed as evidenced by ^1H NMR spectroscopy. The only observed product was acetone, and unreacted diazoalkane **2θ** was reisolated.

1-Diazo-3,5-dimethylcyclohexa-2,5-dien-4-one (2η).[21] According to the general procedure 20.0 mg (0.227 mmol) of dioxetane **1a** and 27.3 mg (0.227 mmol) of diazoalkane **2η** were dissolved in 0.8 mL of deuteriochloroform and allowed to stir at 0 °C for 153 h. After this time the dioxetane was completely consumed as monitored by ^1H NMR spectroscopy, and acetone was the only observed product. Diazoalkane **2η** was reisolated.

Reaction of Dioxetane 1a with Diazoalkane 2δ under Irradiation at 589 nm and 0 °C. Samples of 20.0 mg (0.227 mmol) of dioxetane **1a** and 44.1 mg (0.227 mmol) of diazoalkane **2δ** were dissolved in 0.8 mL of deuteriochloroform at 0 °C and irradiated with two 150-W sodium vapor lamps for 14 h. By ^1H NMR spectroscopy 24% of 2,2-diphenyl-4,4-dimethyl-1,3-diox-

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olane (**3aδ**), 76% acetone, 31% of diphenylacetaldehyde (**5aδ**), and 22% of tetraphenylazine were observed. More than 95% of dioxetane **1a** was consumed.

Reaction of Dioxetane 1a with Diazoalkane 2δ under Irradiation at 589 nm and −40 °C. Samples of 20.0 mg (0.227 mmol) of dioxetane **1a** and 44.1 mg (0.227 mmol) of diazoalkane **2δ** were dissolved in 0.8 mL of deuteriochloroform at 0 °C, cooled to −40 °C, and irradiated with two 150-W sodium vapor lamps for 14 h. By ^{1}H NMR spectroscopy 9% of 2,2-diphenyl-4,4-dimethyl-1,3-dioxolane (**3aδ**), 91% of acetone, 26% of diphenylacetaldehyde (**5aδ**), and 32% of tetraphenylazine were observed. No dioxetane could be detected after this time.

Reaction of Dioxetane 1b with Diazoalkane 2δ. Samples of 200 mg (0.880 mmol) of dioxetane **1b** were dissolved in 25 mL of methylene chloride and cooled to −40 °C. Then 170 mg (0.880 mmol) of diazoalkane **2δ**, dissolved in 5 mL of methylene chloride, was slowly added within 2 min. After 3.5 h the peroxide test was negative and the reaction mixture was allowed to warm to ambient temperature. The solvent was removed at 20 °C/15 Torr, and the product mixture was submitted to silica gel column chromatography by eluting with a 1:3 mixture of methylene chloride/petroleum ether (30–50 °C). The first fraction contained 26.0 mg (7%) of 2-(bromomethyl)-2-phenyloxirane (**6b**) as a colorless oil. The second fraction contained 304 mg (82%) of 4-(bromomethyl)-2,2,4-triphenyl-1,3-dioxolane (**3bδ**), followed by 22.0 mg (6%) of benzophenone. Epoxide **6b** and benzophenone were identified by comparison of their ^{1}H and ^{13}C NMR spectra with authentic samples. Analytically pure 1,3-dioxolane **3bδ** was obtained by recrystallization from a 1:3 mixture of methylene chloride/petroleum ether (30–50 °C).

4-(Bromomethyl)-2,2,4-triphenyl-1,3-dioxolane (3bδ): mp 122–123 °C; colorless needles; TLC [1:3 methylene chloride/petroleum ether (30–50 °C)]; R_f = 0.34; IR (CCl_4) 3085, 3050, 1570, 1455, 1260, 1225, 1095, 1085, 1020, 960 cm^{-1}; ^{1}H NMR ($CDCl_3$) AB pattern (δ_A = 3.51, δ_B = 3.62, J = 10.3 Hz, 2H, CH_2-Br), AB pattern (δ_A = 4.16, δ_B = 4.49, J = 8.8 Hz, 2H, CH_2O), 7.09–7.60 (m, 15H, arom H); ^{13}C NMR ($CDCl_3$) δ 39.7 (t, CH_2Br), 73.3 (t, C-5), 85.2 (s, C-4), 111.5 (s, C-2), 126.2 (d), 126.3 (d), 128.1 (d), 128.2 (d), 128.3 (d), 128.3 (d), 128.5 (d), 140.7 (s), 142.6 (s). Anal. Calcd for $C_{22}H_{19}BrO_2$ (395.3): C, 66.84; H, 4.85. Found: C, 66.84; H, 4.89.

Reaction of Dioxetane 1b with Diazoalkane 2δ in 1:1 Methanol/Methylene Chloride. A sample of 200 mg (0.880 mmol) of dioxetane **1b** was dissolved in 10 mL of a 1:1 mixture of methanol and methylene chloride and cooled to −40 °C. After addition of 170 mg (0.880 mmol) of diazoalkane **2δ**, stirring was continued for 3.5 h. The reaction mixture was allowed to warm to room temperature and the solvent removed at 20 °C (15 Torr). Silica gel column chromatography of the crude product mixture by eluting with a 1:3 mixture of methylene chloride/petroleum ether (30–50 °C) afforded as the first fraction 63.0 mg (17%) of 2-(bromomethyl)-2-phenyloxirane (**6b**), as the second fraction 229 mg (62%) of 1,3-dioxolane **3bδ**, and finally 56.0 mg (15%) of benzophenone.

Reaction of Dioxetane 1c with Diazoalkane 2δ. Samples of 1.00 g (9.79 mmol) of dioxetane **1c** and 1.87 g (9.79 mmol) of diazoalkane **2δ** were dissolved in 25 mL of methylene chloride and stirred for 240 h at 0 °C. Workup and silica gel chromatography by eluting with a 1:4 mixture of methylene chloride/petroleum ether (30–50 °C) afforded as first fraction 36.8 mg (1%) of 4,4,5-trimethyl-2,2-diphenyl-1,3-dioxolane (**3cδ**) and as second fraction 1.40 g (85%) of tetraphenylazine. Analytically pure (**3cδ**) was obtained by recrystallization from petroleum ether (30–50 °C).

4,4,5-Trimethyl-2,2-diphenyl-1,3-dioxolane (3cδ): mp 94–95 °C; white rhombic plates; TLC [1:4 methylene chloride/petroleum ether (30–50 °C)], R_f = 0.27; IR (CCl_4) 3020, 2980, 2910, 2870, 2820, 1454, 1420, 1360, 1345, 1235, 1180, 1140, 1085, 1040, 1005, 930 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.16 (s, 3H, CH_3), 1.28 (d, J = 6.4 Hz, 3H, CH_3), 1.29 (s, 3H, CH_3), 3.81 (q, J = 6.4 Hz, 1H), 7.20–7.40 (m, 6H, arom H), 7.45–7.65 (m, 4H, arom H); ^{13}C NMR ($CDCl_3$) δ = 14.1 (q, CH_3), 22.9 (q, CH_3), 25.1 (q, CH_3), 79.6 (d, C-5), 81.9 (s, C-4), 107.0 (s, C-2), 125.9 (d), 126.1 (d), 127.5 (d), 127.6 (d), 127.9 (d), 144.0 (s), 144.7 (s); exact mass calcd for $C_{18}H_{20}O_2$ m/z = 268.1463, found m/z = 268.1453.

Reaction of Dioxetane 1d with Diazoalkane 2δ. A mixture of 20.0 mg (0.172 mmol) of dioxetane **1d** and 33.4 mg (0.172 mmol) of diazoalkane **2δ** in 0.8 mL of deuteriochloroform was allowed to react at 0 °C. After 400 h, the dioxetane was completely converted into acetone (fragmentation), but no insertion product **3dδ** was observed by ^{1}H NMR spectroscopy of the crude product mixture.

Reaction of Diazoalkane 2δ with Formaldehyde. Through a solution of 50.0 mg (0.257 mmol) of diazoalkane **2δ** in 10 mL of chloroform was passed gaseous formaldehyde by means of a stream of nitrogen gas. After 1 h, the red color of diazoalkane **2δ** had completely disappeared and the solvent was removed at 20 °C (15 Torr). Column chromatography on silica gel by eluting with a 1:10 mixture of methyl *tert*-butyl ether/petroleum ether (30–50 °C) afforded 46.0 mg (91%) of diphenylacetaldehyde (**5aδ**) as a colorless oil. ^{1}H and ^{13}C NMR data were in accordance with those of an authentic sample.

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