Thermally and Photochemically Initiated Radical Chain Decomposition of Ketone-Free Methyl(trifluoromethyl)dioxirane

Waldemar Adam,*,† Ruggero Curci,‡ Maria Elena González Nuñez,† and Rossella Mello†

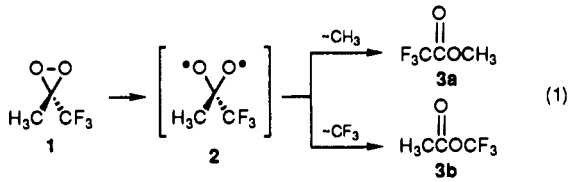
Contribution from the Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-8700, Würzburg, Germany, and CNR Centre MISO, Department of Chemistry, University of Bari, Via Amendola, 173, Bari, Italy-70126. *Received December 3, 1990*

Abstract: Ketone-free solutions of methyl(trifluoromethyl)dioxirane (**1**) were obtained for the first time in several inert solvents, which enabled the study of the thermal and photochemical decompositions of dioxirane **1** in gas, solution, and matrix phases. Vacuum flash pyrolysis of dioxirane **1** afforded exclusively methyl trifluoroacetate (**3a**). Both gas- and liquid-phase photolyses and thermal liquid-phase decomposition of dioxirane **1** involve a radical chain process, initiated by attack of CH_3 and CF_3 radicals on dioxirane **1** to give α-alkoxy-substituted alkoxy radicals as intermediates; the latter are responsible for the production of esters **3a–d**. Matrix-phase photolysis of dioxirane **1** led to methyl trifluoroacetate (**3a**) and 1,1,1-trifluoroethane as main products, while gas-phase pyrolysis gave exclusively the ester **3a**.

Introduction

The recent isolation[1a] of methyl(trifluoromethyl)dioxirane (**1**) in solution of trifluoroacetone from the reaction between its parent ketone and Caroate ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) enabled a number of efficient and selective oxyfunctionalizations of a variety of substrates under mild conditions, even saturated hydrocarbons.[1b] While this preparative chemistry is being actively developed, to date little is known about the photochemical and thermal fate of dioxiranes.

We reported[1a] that brief exposure to UV or even to 586-nm radiation causes the rapid exothermic decomposition of dioxirane **1**, which yielded mainly methyl trifluoroacetate (**3a**), presumably by rearrangement of the intermediary dioxyl diradical **2** (eq 1). A similar reaction path was observed for the parent dioxirane, when generated in the gas-phase ozonolysis of ethylene[2] and in the photolysis of a number of dioxiranes in argon matrices.[3]



(1)

Presently we present our detailed study of the thermal and photochemical decompositions of dioxirane **1** in the gas, solution, and matrix phases. The fact that dioxirane **1** could be obtained for the first time in ketone-free media enabled a careful examination of the product composition, which provided valuable mechanistic insights into the complex decomposition modes of dioxiranes. The salient feature is the disclosure of a radical chain mechanism propagated by α-alkoxy-substituted alkoxy radicals **4**, which are produced by induced decomposition of dioxirane **1**.

Results

Preparation and Properties of Methyl(trifluoromethyl)dioxirane (1) in Ketone-Free Media. Methyl(trifluoromethyl)dioxirane (**1**) was prepared from trifluoroacetone by the reported ketone/Caroate method.[1] Dioxirane **1** was for the first time isolated free of ketone by diluting the freshly prepared dioxirane **1** in trifluoroacetone solution with an appropriate inert solvent (cf. Table I) and extracting the trifluoroacetone in the cold (ca. 0 °C) with doubly distilled water. By this simple method, the trifluoroacetone went into the aqueous phase as its hydrate, while the dioxirane **1** was contained in the organic phase to afford pale yellow solutions, ca. 0.50 M by iodometry. Repetitive freeze-drying cycles at −196 °C and 0.01 Torr permitted to concentrate the ketone-free dioxirane **1** solutions to ca. 0.85 M. Three water washings sufficed, and the loss of dioxirane **1** was at most ca. 10%. Besides the solvents in Table I, also solutions of dioxirane **1** in deuteriochloroform, perfluorohexane, and FC-40 (a mixture of perfluoro ethers, bp 155 °C) were prepared.

Table I. Stability of Methyl(trifluoromethyl)dioxirane (**1**) in Several Solvents

solvent	temp (°C)	time (h)	dioxirane loss[a,b] (%)
CCl_2FCClF_2[c]	−20	96	0
CCl_2FCClF_2[c]	40	2	50
CCl_4	−20	168	5
CCl_4	0	24	15
CCl_4/CF_3COCH_3[d]	0	24	15
CCl_4	60	0.5	45
CH_2Cl_2	−20	168	6

[a] By iodometry. [b] Initial concentration ranging between 0.4 and 0.8 M. [c] Freon 113. [d] As 33:67 mixture.

In chlorinated solvents, e.g., carbon tetrachloride, methylene chloride, or deuteriochloroform, the dioxirane **1** was found to be more soluble than in the perfluorinated solvent C_6F_{14}. Thus, when a solution of dioxirane **1** in C_6F_{14} was shaken with CCl_4, CH_2Cl_2, or $CDCl_3$, all not miscible with C_6F_{14}, the dioxirane **1** went preferentially into the chlorinated solvents.

Regarding the stability of dioxirane **1** in ketone-free media (cf. Table I), the yellow solutions can be stored at −20 °C with only minor loss of dioxirane content. Consequently, trifluoroacetone is not necessary for stable solutions of dioxirane **1** in the inert chloro- and/or fluorocarbons; in fact, dioxirane loss was found to be the same (15% within 24 h) if pure CCl_4 was diluted with trifluoroacetone to result in a 33:67 CCl_4/CH_3COCF_3 solvent mixture. Noteworthy are the data on the stability of dioxirane **1** in Freon 113 at 40 °C (50% loss within 2 h) and in CCl_4 at 60 °C (45% loss within 30 min). These temperatures are the highest at which a dioxirane was handled to date.

Furthermore, dioxirane **1** was found to be quite stable in strong protic acids such as CF_3SO_3H. Thus, after 4 days at 0 °C a 0.5 M solution of dioxirane **1** in a 2:1 $CCl_4/CDCl_3$ solvent mixture that contained 10% of CF_3SO_3H showed no appreciable dioxirane

† University of Würzburg.
‡ University of Bari.

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Table II. Photochemical and Thermal Decomposition of Methyl(trifluoromethyl)dioxirane (**1**)

	reaction conditions				mass	product distribution (%)[b,c]					
entry	method[a]	temp (°C)	time (min)	conversn (%)	balance (%)	$CF_3CO_2CH_3$ (**3a**)	$CH_3CO_2CF_3$ (**3b**)	$CH_3CO_2CH_3$ (**3c**)	CF_3CH_3	CH_3CO_2H	CF_3CO_2H
1	$h\nu$, $\lambda > 254$ nm	ca. 20	10	100	97	18	53	14	<1	*d*	14
2	$h\nu$, $\lambda > 300$ nm	−5	10	100	93	18	50	15	<1	*d*	16
3	$h\nu$, $\lambda > 380$ nm	−5	10	100	96	21	49	14	<1	*d*	15
4	$h\nu$, $\lambda > 300$ nm,[e] matrix phase	−196	165	78	98	51	8	*d*	41	*d*	*d*
5	$h\nu$, $\lambda > 300$ nm,[f] gas phase	ca. 20	30	100		23	15	10	*d*	31	21
6	Δ, dark, in solution	60	50	94	99[g]	17	34	11	*d*	19	15
7	VFP[f]	500		100	100	>98	*d*	*d*	*d*	*d*	*d*

[a] Except for entries 5 and 7, all others were run in a 33:67 $CDCl_3/CCl_4$ solvent mixture; initial concentration of dioxirane **1** ranged from 0.3 to 0.5 M (by iodometry at 0 °C); except for entries 5 and 7, all runs were carried out in a permanently sealed 5-mm NMR tube under argon gas; for entry 1, a quartz NMR tube was used. [b] Product yields were obtained by integration of appropriate ^1H NMR (400 MHz, TMS) and ^{19}F NMR (84 MHz, $CFCl_3$) signals and normalized to 100% conversion; all data are within an error of ca. 5% of the stated values. [c] Except for entry 7, ^{13}C NMR spectra (100 MHz) of all the decomposition mixtures showed the presence of CO_2 as product. [d] Not detected. [e] Sealed NMR tube that contained 0.3 M dioxirane in a 50:50 mixture of CCl_4 and $CDCl_3$ at 77 K under argon gas; liquid nitrogen was used as coolant. [f] Vacuum flash pyrolysis (VFP); the condensed photolysate (entry 5) and pyrolysate (entry 7) were dissolved in $CDCl_3$ for NMR analysis. [g] Including ca. 4% of CF_3COCH_3.

loss by ^1H NMR monitoring. Previously it was reported[4] that dimethyldioxirane[5] is stable toward acetic acid.

We published[1] already the spectral data of dioxirane **1** in trifluoroacetone solution, but take the opportunity here to give the pertinent spectral data for the ketone-free dioxirane **1** (cf. Experimental Section). In the absence of trifluoroacetone, as expected, only minor differences were observed in the ^1H, ^{13}C, and ^{19}F NMR spectra. Furthermore, since both the ^1H and ^{19}F NMR spectra of the ketone-free dioxirane **1** exhibited only traces of trifluoroacetone, a complete IR spectrum in Freon 113 and CCl_4 is also given.

Photochemical Decomposition of Ketone-Free Methyl(trifluoromethyl)dioxirane (1) Solutions. The results of the photolysis of dioxirane **1** in ketone-free solutions under a variety of conditions are shown in Table II. Entries 1–3 of Table II reveal that on photolysis dioxirane **1** led to methyl trifluoroacetate (**3a**), trifluoromethyl acetate (**3b**), and methyl acetate (**3c**) as major products, trifluoroacetone was not formed at all, and 1,1,1-trifluoroethane was observed only in traces (<1%). Within the experimental error, the product distribution was independent of wavelength ($\lambda > 254$, 300, and 380 nm) and temperature (−5 to +20 °C). By means of ^{19}F NMR analysis, significant amounts of trifluoroacetic acid were observed. Noteworthy is the detection of carbon dioxide by ^{13}C NMR analysis in all photolysate mixtures. A control experiment showed the absence of CO_2 in the original solution of the ketone-free dioxirane **1** as well as in a solution treated with diphenyl sulfide to give trifluoroacetone and submission of the resulting reaction mixture to ^{13}C NMR analysis. No significant difference was observed when in a control experiment dioxirane **1** was photolyzed in perfluorohexane at $\lambda > 380$ nm (−5 °C, 10 min) under an argon gas atmosphere; ^1H NMR analysis of the resulting photolysate showed the same product distribution as for entries 1–3 of Table II.

On the other hand, profound differences in the photochemical behavior of ketone-free dioxirane **1** were noted when the irradiations at $\lambda > 380$ nm and −15 °C were carried out under argon versus oxygen gas. Thus, quantitative NMR analysis of the final photolysate showed that under argon gas the dioxirane **1** was totally converted into the esters **3a–c** after 15 min, while under oxygen gas less than 10% was consumed and no definitive products could be detected.

The aggregation state also altered significantly the photochemistry of ketone-free dioxirane **1**. In the matrix-isolated form at $\lambda > 300$ nm and at −196 °C (Table II; entry 4), 78% consumption of dioxirane **1** was achieved within 165 min. Quantitative NMR analysis indicated formation of 1,1,1-trifluoroethane (41%) and ester **3a** (51%); only a small amount of ester **3b** (8%) and no trifluoroacetone were detected. The photolysate contained CO_2, as confirmed by ^{13}C NMR.

Gas-phase photolysis of ketone-free dioxirane **1** at ca. 20 °C and ca. 52 Torr (Table II; entry 5) led to complete consumption of dioxirane **1** within 30 min, and NMR analysis revealed that the esters **3a–c** (48%) and trifluoroacetic acid (21%) were formed as products. By ^{13}C NMR, CO_2 was also detected, but no trifluoroacetone was found. The significant amount of acetic acid (31%), detected in the photolysate, was demonstrated to come from the hydrolysis of ester **3b** under the experimental conditions. No 1,1,1-trifluoroethane could be detected.

Thermal Decomposition of Ketone-Free Methyl(trifluoromethyl)dioxirane (1) Solutions. The thermolysis of ketone-free dioxirane **1** in 33:67 $CDCl_3/CCl_4$ solvent mixture was carried out in the dark at 60 °C (Table II; entry 6). After 50 min, NMR analysis showed ca. 94% conversion of dioxirane **1** and besides the esters **3a–c** (6%) formed as major products, also a small amount of trifluoroacetone (4%), trifluoroacetic acid (15%), and CO_2 (by ^{13}C NMR) were detected. The acetic acid (19%) was demonstrated to originate from the hydrolysis of trifluoromethyl ester **3b** under the experimental conditions as above, reported in entry 5 of Table II. Vacuum flash pyrolysis at ca. 500 °C and 0.002 Torr led to methyl trifluoroacetate (**3a**) as the exclusive product (Table II; entry 7). Control experiments confirmed that all products formed in the solution thermolysis (Table II; entry 6) were stable toward the vacuum flash thermolysis conditions.

Trifluoromethyl Acetate (3b). All products in Table II are known compounds, and they were identified in the photolysates of dioxirane **1** by direct comparison with the original commercial products. Ester **3b** is an unknown compound and was spectroscopically characterized directly in the photolysate of dioxirane **1**. The ^1H, ^{19}F, and ^{13}C NMR spectral data (cf. Experimental Section) all support the proposed structure. We observed a singlet at $\delta = 2.18$ in the ^1H NMR spectrum (200 or 400 MHz) and in the ^{13}C NMR spectrum (100 MHz) a singlet at $\delta = 20.7$, a quartet at $\delta = 119.2$ ($J_{CF} = 265.6$ Hz) and, for the carbonyl resonance, a singlet at $\delta = 162.1$. The carbonyl stretching frequency at 1824.2 cm^{-1} provides evidence for the stronger C=O bond in ester **3b**. Ester **3b** was found to undergo hydrolysis to acetic acid, as confirmed by ^1H NMR analysis. Also traces of CF_3OH were detected in the ^{19}F NMR spectra of the dioxirane **1** photolysate, as evidenced by its characteristic $\delta = -54.0$ resonance.[6] The esters **3a** and **3b** in the photolysates of dioxirane **1** could not be separated even by capillary GC; nevertheless, a mass spectrum of both esters showed a very intense parent ion ($m/z = 128$) attributed to

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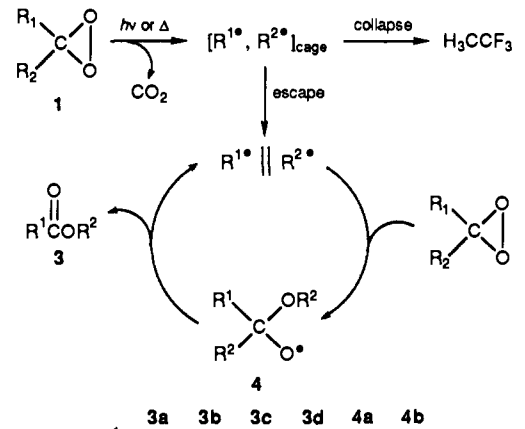
Scheme I



	3a	3b	3c	3d	4a	4b
R^1	CF_3	CH_3	CH_3	CF_3	CF_3	CH_3
R^2	CH_3	CF_3	CH_3	CF_3	CH_3	CF_3

$[CH_3COOCF_3]^+$, in contrast with the GC–MS spectrum of an authentic sample of ester **3a**, in which the molecular ion $[CF_3COOCH_3]^+$ was found in less than 1% abundance.

Discussion

The preparation of ketone-free solutions of methyl(trifluoromethyl)dioxirane (**1**) in inert solvents (Table I) by the simple trick of removing the trifluoroacetone as hydrate permitted for the first time a detailed product study of the thermal and photochemical decompositions, a necessity for mechanistic insight. Even only a cursory look at the product data in Table II reveals some surprising features. For example, the appreciable amounts (10–15%) of methyl acetate (**3c**) in essentially all modes of decomposition (Table II; entries 1–3, 5, and 6) cannot be reconciled in terms of the proposed rearrangement of the dioxyl diradical in eq 1.[2,3,7]

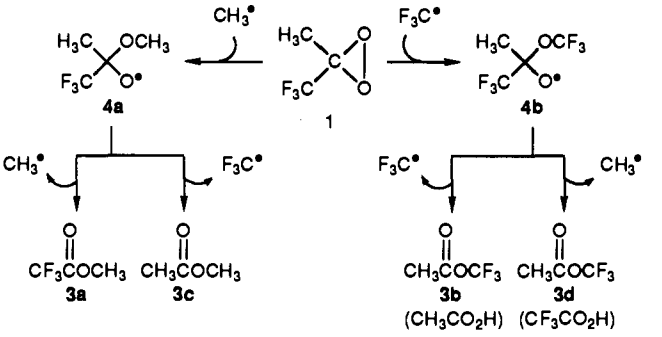
The fact that coupling products such as CH_3–CF_3 were detected, and even large quantities (41%) were produced in the matrix phase photolysis (Table II; entry 4), points clearly to the formation of free radicals. Moreover, the fact that in the presence of oxygen gas the rate of decomposition is significantly retarded in the photolysis of dioxirane **1** and the formation of ester products **3** is inhibited is a strong indication that radical chain reactions are involved in the dioxirane decomposition.

On the basis of these experimental observations, we propose for all modes, except the matrix-phase photolysis (Table II; entry 4) and the pyrolysis (Table II; entry 7), the radical chain mechanism in Scheme I. Such induced decompositions are well established in the photolysis[8] and thermolysis[9] of peroxides in solution as well as gas phase.[10]

Thus, photochemical and thermal activation lead to CO_2, which was observed (cf. Table II, footnote *c*), and the caged radical pair $[R^{1\bullet}, R^{2\bullet}]$. Radical coupling affords the 1,1,1-trifluoroethane, and escape leads to the free $CH_3^\bullet$ and $CF_3^\bullet$ radicals. These in turn attack the dioxirane **1** to generate the α-alkoxy-substituted alkoxy radicals **4**; β-scission of the latter leads to the esters **3** and the $CH_3^\bullet$ and $CF_3^\bullet$ radicals, which propagate the chain.

The observation that molecular oxygen retards the rate of the photolysis implies that O_2 scavenges the initiating radicals $CH_3^\bullet$ and $CF_3^\bullet$ and consequently inhibits the chain process depicted in Scheme I. The fact that in the photolytic decomposition of dioxirane **1** in the presence of dioxygen no ester products **3** could be detected (although slow consumption of the dioxirane **1** took place to afford a complex, intractable product mixture (by NMR and GC)) indicates that the source of ester products **3** in the radical chain decomposition (Scheme I) derives essentially exclusively from the alkoxy radicals **4**. Therefore, the rearrangement of the dioxyl diradicals **2** plays no significant role in the formation of esters **3** during the radical chain process of Scheme I, so that the product distribution among the esters **3** must be reconciled in terms of the chemistry of the α-alkoxy-substituted alkoxy radicals **4**.

Scheme II



	ester distribution (%)[b]				dioxirane attack by		total β-scission of	
entry[a]	3a	3c	3b	3d[d]	$CH_3^\bullet$ 3a + 3c	$CF_3^\bullet$ 3b + 3d	$CH_3^\bullet$ 3a + 3d	$CF_3^\bullet$ 3b + 3c
1	18	14	53	14	32	67	32	67
2	18	15	50	16	33	66	34	65
3	21	14	49	15	35	64	36	63
5	23	10	46	21	33	67	44	56
6	17	11	53	15	28	68	32	64

[a] For ease of comparion, these entries are the same as those in Table II. [b] The ester distribution is based on the relative product yields in Table II; the error is ca. 5% of the stated values. [c] Yield of CH_3CO_2H was added to correct for hydrolysis of ester **3b**; yield of $CF_3CO_2H_2$ was taken as yield of ester **3d** as the result of hydrolysis.

Before entering into details, attention must be focused on the appreciable amounts of acetic and trifluoroacetic acids in the various decompositions (Table II). We observed during the isolation of the hydrolytically labile trifluoromethyl acetate (**3b**) appreciable hydrolysis to acetic acid; we also detected traces of CF_3OH by ^{19}F NMR. The latter has been reported[6] as an extremely labile substance, which dissociates into HF and $F_2C{=}O$. In view of these results, we propose that also trifluoroacetic acid derives from adventitious hydrolysis of trifluoromethyl trifluoroacetate (**3d**). The latter is a hitherto unknown substance that could not be detected by ^{19}F NMR and capillary GC–MS in the decomposates of dioxirane **1**, presumably due to its expected high volatility and ease of hydrolysis. Consequently, like acetic acid, which derives from hydrolysis of $CH_3CO_2CF_3$ (**3b**), trifluoroacetic acid is correspondingly produced principally from hydrolysis of $CF_3CO_2CF_3$ (**3d**). Thus, the yields of trifluoromethyl ester products **3b** and **3d** should be corrected for hydrolysis. In Scheme II are shown the mechanistic details of the ester **3** forming steps from β-scission of the alkoxy radicals **4** for the various decomposition modes, which are subject to the radical chain mechanism in Scheme I with the exception of the matrix photolysis and the vacuum flash pyrolysis. From the product data of Table II, the ester **3a–d** distributions, the extent of attack by $CH_3^\bullet$ and $CF_3^\bullet$ radicals on the dioxirane **1**, and the extent of $CH_3^\bullet$ and $CF_3^\bullet$ β-scission in the alkoxy radicals **4** were computed; these are summarized in tabular form in Scheme II.

The extent of attack by the $CH_3^\bullet$ and $CF_3^\bullet$ radicals on the dioxirane **1** in the important propagation step of this radical chain process (Scheme I) is reflected by the sum of methyl esters **3a** and **3c** versus the sum of trifluoromethyl esters **3b** and **3d**. The attack by $CF_3^\bullet$ on the peroxide bond dominates by ca. 2-fold (cf. Scheme II), which is not surprising in view of the generally higher reactivity of trifluoromethyl radicals.[11] In fact, one would have

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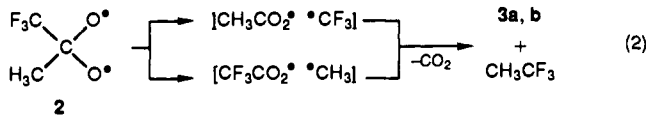
expected a greater differentiation, but these induced reactions should be quite fast (probably diffusion-controlled) for the strained dioxiranes, so that the selectivity must be low. Moreover, the expected more pronounced attack by $CF_3^\bullet$ versus $CH_3^\bullet$ radicals on the dioxirane is offset by the diminished ease of β-scission for the CF_3 versus CH_3 substituents in the alkoxy radicals **4** (vide infra), and our data reflect the sum of these two opposing trends.

More surprising is the fact that the total extent of β-scission of the alkoxy radicals **4** also dominates for the CF_3 radical by about 2-fold (cf. Scheme II). On the basis of what is known for the fragmentation of alkoxy radicals,[12] the methyl radical should be cleaved off much in preference compared to the trifluoromethyl radical; however, no data appear to be reported on the β-scission of α-alkoxy-substituted alkoxy radicals **4**. It would be of interest to investigate the chemistry of such α-alkoxy-substituted alkoxy radicals, but unfortunately the necessary peroxidic precursors are not readily accessible.

As expected, the radical chain process (Schemes I and II) does not operate to any significant degree in the matrix-phase photolysis of dioxirane **1** (Table II; entry 4). Already noted was the high yield (41%) of the coupling product CH_3CF_3, but also the lack of the symmetrical esters, i.e., methyl acetate (**3a**) and trifluoromethyl trifluoroacetate (**3d**), is of mechanistic relevance. Therefore, the ester products **3a,b** may arise either by rearrangement of the dioxyl diradical **2** (eq 1) or by β-scission followed by in-cage coupling of the resulting acetyloxy and methyl radical pairs (eq 2).



(2)

Similarly, also in the pyrolysis experiment (Table II; entry 7), the radical chain process (Scheme I) does not operate, because methyl trifluoroacetate (**3a**) is formed exclusively. Not even traces of the radical chain derived esters **3c,d** and the coupling product CH_3CF_3 were detected. Thus, exclusive methyl migration is the preferred process in the rearrangement of the dioxyl diradical **2** (eq 1) to give the methyl ester **3a** in the pyrolysis. This can readily be reconciled in terms of the greater propensity to cleave off methyl versus trifluoromethyl radicals in view of the respective bond energies.

In summary, the thermal and photochemical decomposition of methyl(trifluoromethyl)dioxirane (**1**) is a complex process, but its mechanistic details could be explored by the fact that ketone-free solutions of dioxirane **1** were made available. The cleanest transformation is the vacuum flash pyrolysis, which gives the exclusive formation of methyl ester **3a**. The matrix-phase photolysis of dioxirane **1** generates acetyloxy–alkyl radical pairs as precursors to the esters **3a,b** and CH_3CF_3 as an in-cage coupling product. Finally, all remaining modes of decomposition, i.e., solution thermolysis and solution- and gas-phase photolyses of the dioxirane **1**, involve the radical chain process in Scheme I. The initiating step is the β-alkyl scission of the dioxyl diradical **2**, and the important propagating step is attack of the alkyl radicals on the dioxirane **1** to lead to α-alkoxy-substituted alkoxy radicals **4a,b**; the latter serve as the precursors to the ester products **3a–d** by β-alkyl fragmentation.

Experimental Section

General Aspects. Instrumentation for spectra: infrared (IR) spectra; Perkin-Elmer 1420 and Nicolet 7000 FT IR; ^{1}H NMR spectra, Bruker AC 200 (200 MHz) or Bruker WM 400 (400 MHz); ^{13}C NMR spectra, Bruker AC 200 (50 MHz) and Bruker WM 400 (100 MHz); ^{19}F NMR spectra, Bruker WH 90 (84 MHz); mass spectra (MS), 8200 Finnigan MAT (70 eV) connected to a 3700 Varian gas chromatograph.

Solvents and compounds that were used in product analyses were purified according to standard literature procedures. The purified solvents methylene chloride, 1,1,2-trifluoro-1,2,2-trichloroethane, carbon tetrachloride, deuteriochloroform, deuteriomethylene chloride, perfluorohexane, and 1,1,1-trifluoro-2-propanone (Fluka) were deaerated and stored under dry inert argon gas. The triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (Caroate), a gift from Degussa AG, Hanau, Germany, was used as received.

Photolyses were carried out either in a Rayonet Photochemical Reactor RP 100 (75 W, 250 V), Southern New England Ultraviolet Co., equipped with 300- and 350-nm lamps, or by irradiating with a mercury high-pressure arc (150 W), provided with Pyrex glass ($\lambda > 300$ nm) or KV 380 ($\lambda > 380$ nm) filters. Capillary GC was performed on a Fractovap 4100 (Carlo Erba Co.), equipped with Fl detector and a OV Ol capillary column (60-m, film thickness 0.25 μm, i.d. 0.32 mm).

Isolation of Methyl(trifluoromethyl)dioxirane (1) in Ketone-Free Media. Methyl(trifluoromethyl)dioxirane (**1**) was prepared from trifluoroacetone (Fluka, bidistilled over P_2O_5) by the reported[1] ketone/Caroate method. To the 0.5–0.85 M (standardized by iodometry) yellow solution of **1** in the parent ketone was added about an equal volume of the desired inert solvent and washed with the double volume of bidistilled water (over $KMnO_4$) at low temperature (ca. 0 °C) in a jacketted separatory funnel. The parent ketone went quickly into the aqueous phase, while the ketone-free dioxirane **1** was contained in the organic phase. The organic layer with the dioxirane **1** was dried briefly over $MgSO_4$, quickly filtered, and stored over 4-Å molecular sieves at −20 °C in the dark (Table I). ^{1}H NMR (2:1 or 1:1 $CCl_4/CDCl_3$ or 2:1 or 1:1 $CF_2ClCFCl_2/CDCl_3$, 400 MHz, 0 °C): δ 1.95 (q, $J_{HF} = 1.2$ Hz). ^{19}F NMR (2:1 or 1:2 $CCl_4/CDCl_3$, $CFCl_3$, 84 MHz, 0 °C): δ −81.4 (s). IR ($CF_2ClCFCl_2$): ν 3020 (w) cm^{-1}, 1447 (m), 1427 (m), 1402 (s), 1330 (s), 755 (m), 745 (m), 715 (s), 615 (s). IR (CCl_4): ν 3018 cm^{-1}, 1460, 1430, 1408, 1385, 1230, 660.

Further Concentration of the Solutions of Dioxirane 1 in Ketone-Free Media. Solutions of dioxirane **1** in a particular solvent (Table I) were further concentrated through freeze-drying by allowing a frozen (liquid nitrogen) CCl_4 solution of dioxirane **1** to evaporate slowly at $<10^{-2}$ Torr and condensing the effluent in a cold trap kept at liquid nitrogen temperature. In a standard run, from 3 mL of a starting 0.6 M solution of dioxirane **1** in CCl_4, 2 mL of a 0.85 M solution was obtained.

General Procedure of the Photolysis of Dioxirane 1 in Ketone-Free Solutions. Photolysis of a ca. 0.4 M solution of dioxirane **1** in a 33:67 $CDCl_3/CCl_4$ solvent mixture, which contained an inert standard (for ^{1}H NMR the $CHCl_3$ impurity in the $CDCl_3$ and for ^{19}F NMR $CFCl_3$ were used), was carried out under argon gas in permanently sealed 5-mm NMR tubes, thermostated by using a jacketted condenser, which was supplied with ethanol coolant from a RK 20 Lauda cryostat. The final photolysate was submitted to quantitative NMR analysis, and the results are given in Table II.

To determine the mass balance, an aliquot of the same stock solution of dioxirane **1** (ca. 0.25 mmol), which was used for the photolysis, was treated with diphenyl sulfide (0.15 mmol), quickly transferred into a 5-mm NMR tube, sealed permanently under argon gas, and submitted to ^{1}H, ^{13}C, and/or ^{19}F NMR quantitative analysis. The ratio between the electronic integrals of the trifluoroacetone, produced in the Ph_2S oxidation, and the internal standard was measured. This value was compared to the sum of the ratios of the photolysis products to the internal standard and from that the mass balance (%) calculated.

Photolysis of Ketone-Free Dioxirane 1 under Oxygen or Argon Gas. Photolyses of ca. 0.4 M solutions of dioxirane **1** in 33:67 $CDCl_3/CCl_4$ solvent mixture were carried out in thermostated 5-mm NMR tubes by gently bubbling oxygen or argon gas through the solution. The final photolysate was submitted to quantitative NMR analysis.

Photolysis of Ketone-Free Dioxirane 1 in Perfluorohexane. Photolysis of ca. 0.4 M solution of dioxirane **1** in perfluorohexane was carried out in a thermostated 3.5-mm NMR tube under argon gas; deuteriobenzene was used as external standard for the quantitative ^{1}H NMR analysis.

Gas Phase Photolysis of Ketone-Free Dioxirane 1. A solution of dioxirane **1** in CCl_4 (ca. 2 mL, 0.85 M) was allowed to evaporate into a cylindrical glass vessel (ca. 300 mL) at ca. 4×10^{-6} Torr (oil diffusion pump) and the final pressure adjusted to ca. 52 Torr. The vessel was irradiated at $\lambda > 300$ nm in the Rayonet photochemical reactor. Subsequently the photolysate was condensed at ca. 2×10^{-3} Torr into a cold trap at −196 °C and the condensate dissolved in ca. 0.7 mL of $CDCl_3$. This final photolysate solution was submitted to NMR analysis, and the results are given in Table II.

Vacuum Flash Pyrolysis of Dioxirane 1. A cylindrical pyrolysis quartz tube (i.d. 1.3 mm, ca. 50 cm long) was connected at one end to a vessel, which contained 3 mL of a 0.5 M solution of **1** in CCl_4, and at the other end to a cold trap kept at −196 °C for collecting the pyrolysate. When a vacuum of ca. 2×10^{-3} Torr was applied, the dioxirane **1** was volatilized into the quartz pyrolysis tube, which was externally heated at 500 °C by means of a Nichrome resistance wire. The collected pyrolysate was

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dissolved in $CDCl_3$ and submitted to NMR analysis. The results are given in Table II.

For quantitative analysis, a ca. 0.4 M solution of dioxirane **1** in a 33:67 solvent mixture of $CDCl_3/CCl_4$, which contained the internal standard (the $CHCl_3$ impurity in the $CDCl_3$ solvent for ^1H NMR and $FCCl_3$ for ^{19}F NMR), was submitted to NMR analysis prior to pyrolysis. Afterward, 0.5 mL of this solution was pyrolyzed and subsequently the pyrolysate again submitted to NMR analysis. The ratios of the electronic integrals of the starting dioxirane to the standard and of the final ester **3a** to the standard were the same within experimental error.

As a control experiment, ca. 0.5 M solution of dioxirane **1** in a 67:33 $CCl_4/CDCl_3$ solvent mixture, contained in a permanently sealed, 5-mm NMR tube under argon gas, was irradiated at $\lambda > 300$ nm by means of a mercury high-pressure arc at −5 °C for 10 min. After completion of the reaction, the photolysate solution was pyrolyzed under the same conditions as above, and the pyrolysate analyzed by ^1H NMR. All the pyrolysis products of the dioxirane **1** were found to be stable under the pyrolysis conditions.

3,3,3-Trifluoromethyl acetate (3b) was characterized directly in the photolysate of dioxirane **1** (as mixture with ester **3a**) in 67:33 $CCl_4/CDCl_3$. ^1H NMR (400 MHZ): δ 2.18 (s). ^{13}C NMR (100 MHz): δ 20.7 (s), 119.2 (q, J_{CF} = 265.6 Hz), 162.1 (s). ^{19}F NMR (84 MHz, $CFCl_3$): δ −58.3 (s). IR: 1824.3 cm^{-1} (C=O). GC-MS (70 eV): *m/z* (%) 128 (12.9) [M^+], 97 (1.4) [CF_3O^+], 69 (100) [CF_3^+], 59 (46.2) [CH_3COO^+], 43 (41.3) [CH_3CO^+]; GC (OV O1, 60-m capillary column, film thickness 0.25 μm, i.d. 0.32 mm, isotherm 45 °C, T_{inj} = 150 °C, T_{det} = 200 °C, N_2 pressure = 0.4 kg/cm^2); R_t = 7.75 min.

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The Electronic Structure and Second-Order Nonlinear Optical Properties of Donor–Acceptor Acetylenes: A Detailed Investigation of Structure–Property Relationships

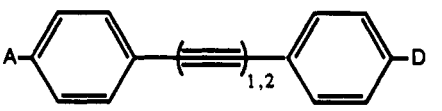
A. E. Stiegman,*,† Eva Graham,† Kelly J. Perry, Lutfur R. Khundkar,†,§ L.-T. Cheng,*,‡ and Joseph W. Perry*,†

Contribution from the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, and the Central Research and Development Department, E.I. du Pont de Nemours & Co., Inc., Experimental Station, P.O. Box 80356, Wilmington, Delaware 19880-0356. *Received February 20, 1991. Revised Manuscript Received May 15, 1991*

Abstract: A series of donor–acceptor acetylene compounds was synthesized in which systematic changes in both the conjugation length and the donor–acceptor strength were made. The effect of these structural changes on the spectroscopic and electronic properties of the molecules and, ultimately, on the measured second-order molecular hyperpolarizabilities (β) was investigated. It was found that increases in the donor–acceptor strength resulted in increases in the magnitude of β. For this class of molecules the increase is dominated by the energy of the intramolecular charge-transfer transition, while factors such as the ground to excited-state dipole moment change and the transition-moment integral are much less important. Increasing the conjugation length from one to two acetylene linkers did not result in an increase in the value of β; however, β increased sharply in going from two acetylenes to three. This increase is attributed to the superposition of several nearly isoenergetic excited states.

The use of organic materials for nonlinear optics applications is an area of considerable recent activity. Interest in these materials is due primarily to their inherent synthetic flexibility which, in principle, permits the "engineering" of molecular properties that will maximize particular nonlinear optical characteristics.[1] For this to be realized it is necessary to understand in detail how and to what extent changes in the electronic structure of a molecule, brought about by synthetic modification, affect the molecular second- and third-order nonlinear polarizabilities. This is required if successful "engineering" of these properties is to be accomplished.

We present here a detailed study of the relationship between the electronic structure and the microscopic second-order nonlinear polarizability for the series of donor–acceptor phenylacetylene compounds having the general structure shown below (where D and A are an electronic donor and acceptor group respectively).



For this series, systematic changes in the conjugation length and in the donor–acceptor group can be readily accomplished with the effect of these changes on the second-order hyperpolarizability determined. From this, an understanding of which changes result in the most significant enhancement of the hyperpolarizability can be deduced.

This series of compounds was also screened for SHG (second harmonic generation) activity. SHG is a macroscopic second-order nonlinear optical property that requires, in crystalline materials, not only significant molecular hyperpolarizabilities but also

† Jet Propulsion Laboratory.
‡ E.I. du Pont de Nemours & Co.
§ NRC–NASA Resident Research Associate, current address: Dept. of Chemistry, Northeastern University, Boston, MA.

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