

Influence of Electron-Donor Sensitizers on SET-Promoted Photochemical Reactions of β,γ -Unsaturated Aldehydes

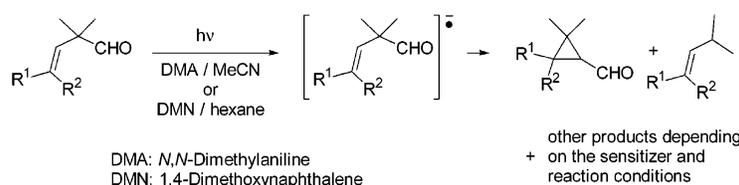
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ABSTRACT



β,γ -Unsaturated aldehydes undergo photochemical oxa-di- π -methane and decarbonylation reactions using DMN as an electron-donor sensitizer, whereas, using DMA, other photoproducts resulting from proton abstraction by ketyl- and alkene-centered radical-anions are also obtained.

Radical-ions, generated from organic molecules by single-electron transfer (SET), are important intermediates in a variety of chemical reactions, particularly, in cyclization processes that lead to the construction of a variety of carbo- and heterocyclic ring systems.^{1,2} Radical-ion intermediates can be generated by ground-state single-electron transfer oxidations and reductions and by photoinduced electron transfer (PET) either directly or by using electron-donor and electron-acceptor sensitizers.³ As part of our studies in this area, we have observed that 1-aza-di- π -methane (1-ADPM) rearrangements take place through radical-cation intermediates. For example, sensitized irradiation using the electron-acceptor sensitizer 9,10-dicyanoanthracene (DCA) of a series of 1-aza-1,4-diene derivatives leads to formation of the corresponding cyclopropanes.⁴ In another effort, we found

that 2-aza-1,4-diene radical-cations, generated under these photosensitized conditions, undergo 2-aza-di- π -methane (2-ADPM) reactions affording *N*-vinylaziridines.⁵

In contrast to the large number of studies focusing on SET photocyclizations that take place via radical-cation intermediates, those exploring radical-anions as intermediates in these reactions have received much less attention.³ There are only a few examples in the literature of intramolecular reductive cyclization reactions via radical-anions other than ketyl.³ However, we have recently reported 1-ADPM and di- π -methane (DPM) reactions that occur via radical-anion intermediates. For example, irradiation of a series of β,γ -unsaturated imines such as **1** and the 1,4-diene **3** using *N,N*-dimethylaniline (DMA) as an electron-donor sensitizer, leads to production of cyclopropanes **2** and **4**, respectively (Scheme 1).⁶ Because di- π -methane rearrangements have been con-

(1) For a comprehensive review on electron-transfer processes, see: *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001; Vols. 1–5.

(2) For other reviews see: (a) *Photoinduced Electron-Transfer I, II, III, IV and V*. In *Top. Curr. Chem.*; Mattay, J., Ed.; Springer-Verlag: Berlin, 1993; Vols. 156, 158, 159, 163, and 168, respectively. (b) *Electron-Transfer I and II*. In *Top. Curr. Chem.*; Mattay, J., Ed.; Springer-Verlag: Berlin, 1996; Vols. 169 and 177, respectively.

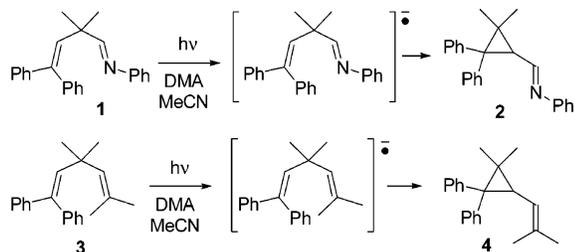
(3) Hintz, S.; Heidebreder, A.; Mattay, J. *Radical Ion Cyclizations*. In *Top. Curr. Chem.*; Mattay, J., Bassi, R., Eds.; Springer-Verlag: Berlin, 1996; Vol. 177, pp 77–124 and references cited therein.

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(5) (a) Armesto, D.; Caballero, O.; Amador, U. *J. Am. Chem. Soc.* **1997**, *119*, 12659–12660. (b) Armesto, D.; Caballero, O.; Ortiz, M. J.; Agarrabeitia, A. R.; Martin-Fontecha, M.; Torres, M. R. *J. Org. Chem.*, **2003**, *68*, 6661–6671.

(6) Armesto, D.; Ortiz, M. J.; Agarrabeitia, A. R.; Martin-Fontecha, M. *J. Am. Chem. Soc.* **2001**, *123*, 9920–9921.

Scheme 1. Examples of 1-ADPM and DPM Rearrangements via Radical-Anion Intermediates

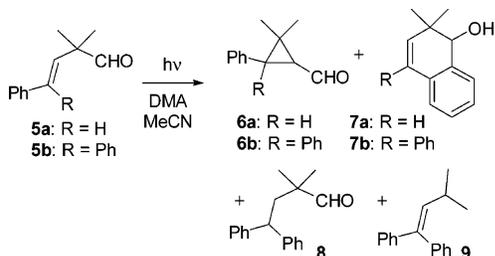


considered for many years to be the paradigm of reactions that take place in the excited state of organic molecules, the observation that these processes can take place in ground-state radical-ion intermediates has opened new lines of research in this area.

In an extension of this effort, we have investigated DMA electron-donor-sensitized photoreactions of a series of β,γ -unsaturated aldehydes that are structurally related to the previously studied 1-aza-1,4-dienes and the 1,4-diene. All of the aldehydes probed in this investigation undergo efficient oxa-di- π -methane (ODPM) rearrangement on triplet-sensitized irradiation.

Irradiation of a solution of (*E*)-**5a**⁷ in acetonitrile containing DMA as an electron-donor sensitizer for 10 min, using a 125 W medium-pressure Hg arc lamp, followed by column chromatography on silica gel, gave recovered **5a** (52%) as a 1:1 mixture of *E*:*Z* isomers and two photoproducts, identified as the cyclopropanecarbaldehyde **6a**⁸ (12%) and dihydronaphthalene derivative **7a** (4%) (Scheme 2). The study

Scheme 2. DMA-Sensitized Irradiations of Aldehydes **5**



was extended to aldehyde **5b**.⁹ DMA-sensitized irradiation of **5b** in acetonitrile, using a 400 W medium-pressure Hg arc lamp, for 90 min yielded **6b**¹⁰ (4%), **7b** (10%), recovered starting material (17%), and two new compounds, characterized as the saturated aldehyde **8** (10%) and the alkene **9**⁷ (10%) (Scheme 2). These results demonstrate that, like their

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(8) Armesto, D.; Ortiz, M. J.; Romano, S.; Agarrabeitia, A. R.; Gallego, M. G.; Ramos, A. *J. Org. Chem.* **1996**, *61*, 1459–1466.

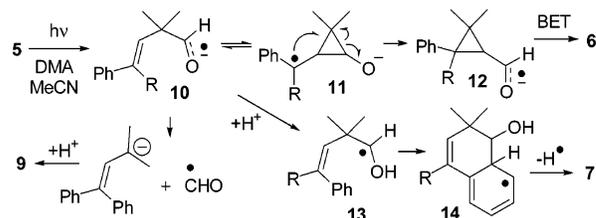
(9) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6259–6267.

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1-aza-1,4-diene and 1,4-dienes analogues, β,γ -unsaturated aldehydes **5** also undergo di- π -methane-type rearrangements via radical-anion intermediates.

Possible mechanistic pathways for formation of **6** and **7** involve the intermediacy of radical-anions **10**, which undergo bonding to give the cyclopropane ring-containing radical-anions **11**. Rearrangement of **11** affords **12**, which by back-electron transfer (BET) generates **6**. The reversibility of the step leading to **11** would account for the observed C–C double-bond isomerization of **10a**. Alternatively, radical-anions **10** can be protonated to afford radicals **13** that cyclize generating intermediates **14**, which lose hydrogen atoms to yield **7** (Scheme 3).

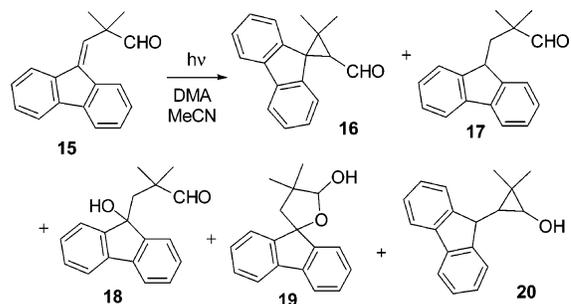
Scheme 3



Compound **8** is formed by a conventional radical-anion reduction of the alkene unit.³ This result is surprising since the carbonyl group should be a better electron-acceptor than the alkene moiety. However, the stabilization provided by diphenyl substitution in **5b** promotes the competitive generation of alkene- and ketyl-centered radical-anions. The formation of **9** in the irradiation of **5b**, possibly by the path shown in Scheme 3, is the first example of a decarbonylation reaction in β,γ -unsaturated aldehydes via radical-anion intermediates.

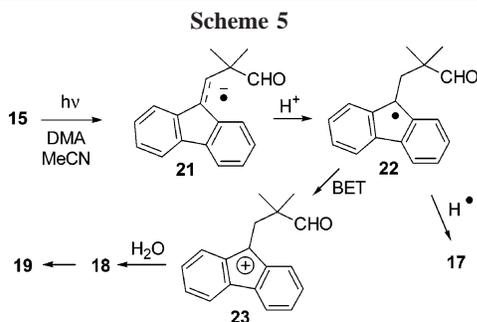
The study was extended to aldehyde **15**.¹¹ Irradiation of **15** for 30 min, under the same conditions used for **5b**, followed by chromatography, afforded recovered **15** (11%) and five other photoproducts, identified as spirocyclopropane derivative **16**¹¹ (1%), saturated aldehyde **17** (8%), γ -hydroxyaldehyde **18** (13%), spirodihydrofuran **19** (16%), and cyclopropanol **20** (4%) (Scheme 4).

Scheme 4



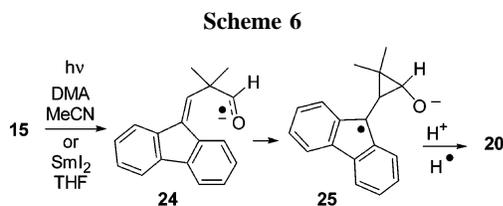
Clearly, compounds **17–19** are formed by way of alkene-centered radical-anion intermediates. Possible mechanistic

pathways for formation of **17–19** involve the intermediacy of radical-anion **21**, the protonation of which yields radical **22**. Hydrogen abstraction by **22** then produces **17**. Alternatively, **22** could participate in BET to give carbocation **23**, which is then trapped by spurious water, always present in acetonitrile, to yield **18**. Finally, cyclization of **18** would form the cyclic hemiketal **19** (Scheme 5). The reasons radical **22**



has this strong tendency to undergo BET to generate carbocation **23** are unclear at this point.

The formation of cyclopropanol **20** is interesting. Although reductive intramolecular cyclization of ketyl radical-anions tethered to a double bond at a suitable distance has been used in the synthesis of different carbo- and heterocycles,¹² there is only one report in the literature of cyclopropane formation by this procedure using β,γ -unsaturated carbonyl compounds.¹³ Cyclopropane **20** could come from radical-anion **21** or from a ketyl radical-anion. To clarify this point, **15** was reacted with SmI_2 in *t*BuOH/THF, affording **20** (61%) exclusively. Earlier efforts have shown that SmI_2 reduces carbonyl groups, but as far as we are aware, it does not promote the generation of radical-anions in simple alkenes.¹² Therefore, the formation of **20** supports the involvement of a carbonyl-centered radical-anion in this cyclization reaction. The mechanism shown in Scheme 6 accounts for the for-



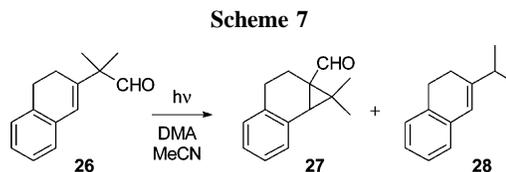
mation of **20**. Thus, the radical-anion **24**, generated thermally or photochemically, can undergo a 3-exo-trig cyclization yielding **25**, which by proton transfer and hydrogen abstraction gives **20**.

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(13) Villar, H.; Guibe, F. *Tetrahedron Lett.* **2002**, *43*, 9517–9520.

Irradiation of aldehyde **26**¹⁴ for 15 min, under the same conditions used for **5b**, after chromatography afforded recovered **26** (30%), cyclopropanecarbaldehyde **27**,⁸ (22%) and alkene **28** (11%) (Scheme 7). In this instance the



formation of products resulting from proton transfer to alkene- or ketyl-centered radical-anions is not observed.

The results outlined above show that radical-anions, generated by DMA-sensitized irradiation of β,γ -unsaturated aldehydes in acetonitrile, undergo ODPM-type rearrangement with variable efficiencies. In addition, a variety of other reactions involving proton abstraction and addition of water have been observed. This is somewhat surprising since DMA-sensitized irradiation of β,γ -unsaturated imines in acetonitrile afford the corresponding 1-ADPM photoproducts, exclusively.⁶

In an attempt to simplify the outcome of these reactions, we have irradiated aldehydes **5a,b**, **15**, and **26** under conditions that minimize proton transfer from the sensitizer radical-cation. A previous study demonstrated that DPM rearrangement of diene **3** via radical-anion intermediates occurs when the reaction is carried out in hexane.⁶ Therefore, **5a,b**, **15**, and **26** were irradiated in hexane, using 1,4-dimethoxynaphthalene (DMN) as an electron-donor sensitizer. As expected, under these conditions formation of products resulting from proton transfer to the alkene and ketyl radical-anions was suppressed (Table 1). Consequently, aldehyde **5a** affords only the ODPM photoproduct **6a**. Compounds **5b**, **15**, and **26** also yield the corresponding cyclopropanes **6b**, **16**, and **27**, respectively, when subjected to these donor-sensitized irradiation conditions. In these instances, alkenes formed by decarbonylation of the corresponding radical-anions were also obtained. Thus, aldehyde **5b** affords alkene **9** as the major product. Compound **15** gives an inseparable mixture of 9-isobutylidene-9*H*-fluorene (**29**) and 9-(2-methylpropenyl)-9*H*-fluorene (**30**). Finally, aldehyde **26** decarbonylates, providing a mixture of alkenes **28** and 2-isopropylidene-1,2,3,4-tetrahydronaphthalene (**31**). The yield of ODPM photoproducts, under these conditions, increases considerably for compounds **15** and **26** but remains practically the same for aldehydes **5a** and **5b**.

In summary, the results arising in this study show that, in a manner similar to 1-aza-1,4-dienes and 1,4-dienes, β,γ -unsaturated aldehydes **5a,b**, **15**, and **26** undergo SET-promoted ODPM rearrangements. These processes are the first examples of ODPM reactions that occur via radical-anion intermediates. However, other products arising by proton transfer to alkene- and ketyl-centered radical-anions are also

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Table 1. Yields of Products in the Irradiation of β,γ -Unsaturated Aldehydes Using DMA and DMN as Electron-Donor Sensitizers

substrate	SET-sensitizer	solvent	ODPM (yield, %)	decarbonylation (yield, %)	C=C reduction (yield, %)	other (yield, %)	starting material (yield, %)
5a	DMA	MeCN	6a (12)			7a (4)	52
5a	DMN	hexane	6a (7)				77
5b	DMA	MeCN	6b (4)	9 (10)	8 (10)	7b (10)	17
5b	DMN	hexane	6b (5)	9 (24)			47
15	DMA	MeCN	16 (1)		17 (8)	18 (13), 19 (16), 20 (4)	11
15	DMN	hexane	16 (25)	29 , 30 (16)			39
26	DMA	MeCN	27 (22)	28 (11)			30
26	DMN	hexane	27 (69)	28 , 31 (6)			20

obtained when the irradiations are promoted by using DMA as an electron-donor sensitizer in acetonitrile. These results contrast those obtained from studies of the reactivity of 1-aza-1,4-diene radical-anions. The latter intermediates undergo the 1-ADPM rearrangement exclusively under these reaction conditions. However, the intervening proton-transfer processes, which result in diminished yields, can be suppressed by using DMN as an electron-donor sensitizer and hexane as a solvent. Under these conditions, competitive decarbonylation reactions are observed for aldehydes **5b**, **15**, and **26**. These are the first examples of reactions that are similar to the well-known Norrish type I process that take place via radical-anion intermediates.

Another interesting observation in this study is the formation of cyclopropanol **20** upon irradiation of aldehyde **15**. There is only one previous report in the literature describing cyclopropane formation by a route involving 3-exo-trig cyclization of radical-anions derived from β,γ -unsaturated carbonyl compounds.¹³ Compound **20** is also obtained in good yield when **15** is reacted with SmI₂ in *t*BuOH/THF.

These results open new lines of research in the area of the β,γ -unsaturated carbonyl compound photochemistry.

Further studies are underway to elucidate the factors that control the photoreactivity of these compounds via radical-anion intermediates.

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Supporting Information Available: Experimental details for the photolysis and the reaction of **15** with SmI₂ and analytical and spectroscopic data for all photoproducts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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