

which would imply either that a Pt-Pt bond exists or that the spread of the bridging C_6F_5 groups (both Pt-C-Pt angles = 74.1°) forces the two Pt atoms to this distance. This is the first case in which a C_6F_5 group has been proved to act as a bridging ligand, but some complexes containing bridging phenyl groups have been structurally characterized.¹² In addition, the Pt-Ag distances, 2.827 (2) and 2.815 (2) Å, together with the fact that there are no ligands serving as bridges across the Pt-Ag edges of the Pt_2Ag triangle, imply that there are also Pt-Ag bonds. Of course, fractional bond orders may well prevail in the Pt-Pt and Pt-Ag bonds. If the Pt and Ag atoms are assigned formal oxidation numbers of II and I, respectively, a total of four electrons would be available for the set of metal-metal bonds.

There are close approaches of ortho F atoms (from the bridging groups) to the silver atom: Ag...F(5), 2.66 (1) Å; Ag-F (10), 2.67 (1) Å. The Pt-C distances to the terminal C_6F_5 groups are 2.02 and 2.06 Å. The Pt-C_{bridge} distances are longer, but they are distinctly unequal (C(1)-Pt(1), 2.28 (2) Å; C(1)-Pt(2), 2.19 (2) Å; C(7)-Pt(1), 2.20 (2) Å; C(7)-Pt(2), 2.28 (2) Å), so that each Pt-C-Pt unit is unsymmetrical. Each C_6F_5 bridging group is practically perpendicular to the Pt_2Ag plane, with dihedral angles of 96.7° and 98.3° . The dihedral angle between Pt(1)-C(1)-Pt(2) and Pt(1)-C(7)-Pt(2) is 30.0° .

Acknowledgment. We thank the CAICYT (Spain) and the U. S. National Science Foundation for support.

Supplementary Material Available: Tables of atomic positional parameters for both structures (7 pages). Ordering information is given on any current masthead page.

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Selectivity and Charge Transfer in Photoreactions of α,α,α -Trifluorotoluene with Olefins[†]

Jochen Mattay,* Jan Runsink, Thomas Rumbach, Cuong Ly, and Joachim Gersdorf

Institut für Organische Chemie der RWTH Aachen
Prof.-Pirlet-Str. 1, D-5100 Aachen, West Germany

Received September 19, 1984

We have recently shown that charge transfer may influence the selectivity of product formation in various bimolecular photoreactions.^{1,2} In extension of these investigations we have studied the photoreactions of α,α,α -trifluorotoluene (**1**) with the olefins **2** and **6** and we have found striking changes in the mode of reaction.³ In this paper we wish to present the first example of C-F bond breakage of α -fluorinated alkyl arenes during a photoaddition reaction.⁴⁻⁷ Furthermore the change of reactivity will

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Scheme 1. Products of Photoreactions between α,α,α -Trifluorotoluene (**1**) and the Olefins **2**

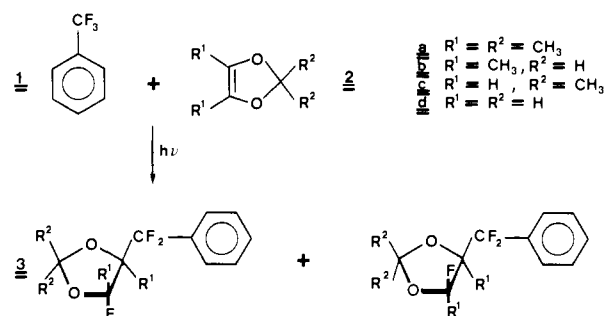


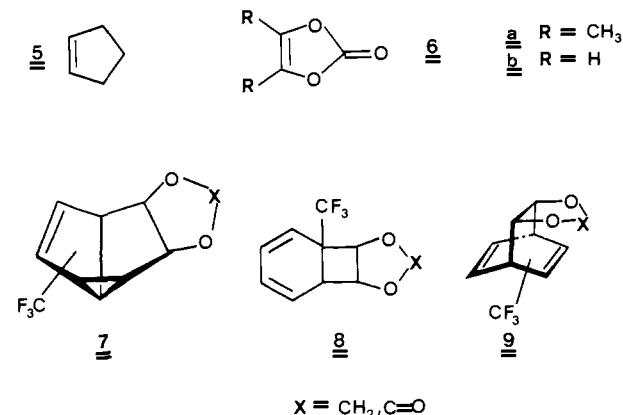
Table I. Free Enthalpies of Electron Transfer and Mode of Photoreactions of α,α,α -Trifluorotoluene (**1**) with Various Olefins

olefin	$E_{1/2}^a$, V	ΔG^b , eV	reaction mode ^c	
			substitution	cycloaddition
2a	+0.42	-0.23	+	-
2b	+0.48	-0.17	+	-
2c	+0.69	+0.04	+	-
2d	+0.76	+0.11	+	ortho, meta
6a	+1.47	+0.82	-	meta
5	+1.83	+1.18	-	meta
6b^d	-2.64	+1.72	-	meta

^a Oxidation (reduction) potentials (vs. Ag/AgNO₃ electrode) were measured by cyclic voltametry (Pt working electrode) in acetonitrile: c(olefin) 1 mmol L⁻¹, c(LiClO₄) 0.1 mol L⁻¹. ^b In dioxane with $E_{1/2}^{red}(1) = -3.18$ V or $E_{1/2}^{ox}(1) = 2.91$ V (consider also note d), $\Delta E_{excit} = 4.65$ eV. ^c (-) + means (no) reaction; ortho (meta) means formation of ortho (meta)cycloadducts. ^d Here **1** acts as the donor and **7** as the acceptor (see text).

be rationalized on the basis of the thermodynamics of electron transfer.

Preparative irradiation ($\lambda = 254$ nm) of 2:1 mixtures in dioxane of **1** and of the olefins **2** and **6** respectively (concentration of **1**: 0.1-0.5 mol L⁻¹) results in formation of products **3**, **4**, and mixtures of ortho, meta, and para cycloadducts **7-9**^{3,4}) in 60-80% yields



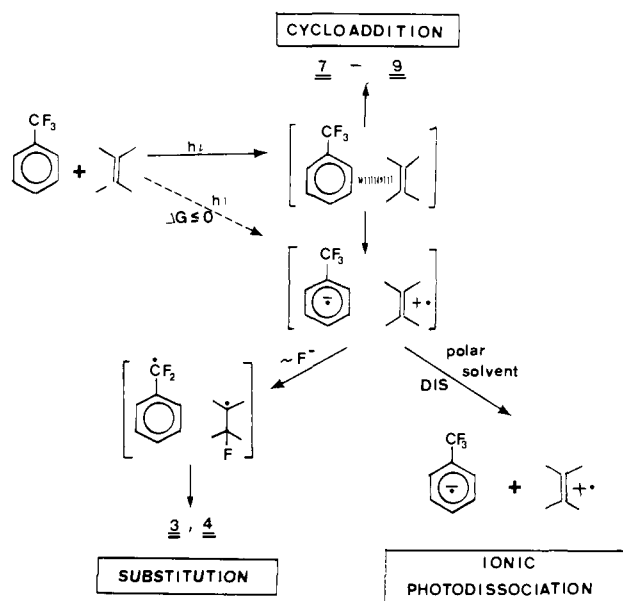
All products were separated by HPLC⁸ and were identified by ¹H and ¹³C NMR. Cornelisse and Osseltson have found the same results in an independent study of the photoreaction of **1** with **6b**.⁹ In general substitution to **3** and **4** is only observed in photoreactions with the 1,3-dioxoles **2**. Whereas **2a-c** only yield the above mentioned products, the weaker donor olefin **2d** already undergoes cycloaddition as the main reaction (90%). This obvious trend is continued in the photoreactions of **5**⁷ and **6**, which exclusively proceed under cycloaddition onto the arene **1**.^{3,4} If it is assumed that the cycloaddition proceeds through a singlet exciplex^{2,10,11}

(8) Chromosorb Si60 column, ethyl acetate-hexane mixture (3-50% ethyl acetate) as eluate.

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Scheme II. Proposed Mechanism of Photoreactions of α,α,α -Trifluorotoluene (**1**) with Olefins



and the substitution takes place via an ion pair as the intermediate analogous to other systems, studied by McCullough,¹² Arnold,¹³ and Lewis,¹⁴ one should expect a dependence of the mode selectivity on the electron transfer enthalpies ΔG . These ΔG values can be easily calculated by means of the Rehm-Weller equation.¹⁵ A simplified version of this equation for 1,4-dioxane (dielectric constant, ϵ 2.2) as solvent is given as follows:

$$\Delta G(\text{eV}) = E_{1/2}^{\text{ox}}(\text{D}) - E_{1/2}^{\text{red}}(\text{A}) - \Delta E_{\text{excit}} + 0.82$$

with $E_{1/2}^{\text{ox}}(\text{D})$ = oxidation potential of the donor, $E_{1/2}^{\text{red}}(\text{A})$ reduction potential of the acceptor, both in acetonitrile, and ΔE_{excit} = excitation energy (here of **1**). The results of such a calculation are shown in Table I and clearly demonstrate that substitution is preferred in systems of exothermic electron transfer. As a consequence these latter systems also exhibit a strong solvent effect; i.e., the quantum yields of product formation decrease by a factor up to 3.5 when changing the solvent polarity from ϵ 2.02 (cyclohexane) to ϵ 37.5 (acetonitrile). These effects may be best rationalized in assuming a competition between product formation and ionic photodissociation, which we have studied in more detail in ketone-olefin systems.^{1,16}

We conclude from these results a mechanism of product formation as shown in Scheme II. The assumption of an exciplex intermediate seems reasonable, even in systems that exhibit exothermic electron transfer, since the rate constants of fluorescence quenching of **1** by olefins do not follow the theoretical curve of direct electron transfer reported by Rehm and Weller.¹⁷

In particular these rate constants are even higher in systems of endothermic electron transfer as shown in Figure 1. Again a more detailed discussion of this phenomenon concerning the luminescence quenching of 1,2-diketones and arenes has been presented elsewhere and will be published soon.¹⁶

Fluorinated ketones like α,α,α -trifluoroacetophenones do show significant charge-transfer quenching as reported by Wagner.¹⁸

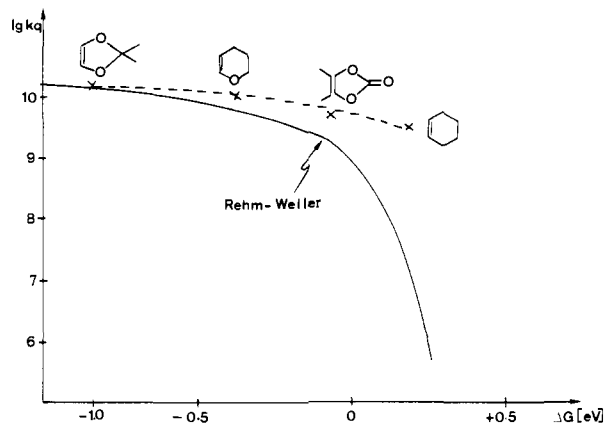


Figure 1. Correlation between measured rate constants of fluorescence quenching of **1** by various olefins (X) and the free enthalpy of radical ion pair formation ΔG in acetonitrile (Rehm-Weller, theoretical curve for electron transfer as the primary step; see ref 17).

However, a similar C-F bond cleavage has not been observed in these systems since ΔG of electron transfer is endothermic according to the Rehm-Weller equation.¹⁹

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and to Prof. Dr. H.-D. Scharf for support of this work. We also gratefully acknowledge some very helpful information concerning the photoreaction of **1** with **6b** from J. Cornelisse, who has independently studied this reaction. J. G. thanks the Studienstiftung des Deutschen Volkes for a predoctoral fellowship.

(19) Even with the strongest acceptor *p*-(trifluoromethyl)- α,α,α -trifluoroacetophenone and toluene as donor ($E_{1/2}^{\text{ox}} = 2.13$ V vs. SCE in CH_3CN) ΔG is positive according to the Rehm-Weller equation.

Evidences for an Efficient Demethylation of Methoxyellipticine Derivatives Catalyzed by a Peroxidase

G rard Meunier[†] and Bernard Meunier^{**††}

Laboratoire de Pharmacologie et de Toxicologie Fondamentales and Laboratoire de Chimie de Coordination, CNRS 31400 Toulouse, France

Received September 18, 1984

Demethylation of methoxylated aromatic compounds usually requires rather drastic reaction conditions in preparative organic chemistry: nitric acid,¹ argentic oxide,² or ceric ammonium nitrate.³ A mild method of aromatic O-demethylation can be still considered as a useful goal for organic synthesis of multifunctional molecules. Whereas easy O- and N-demethylation can be performed by cytochrome P-450 enzymes,⁴⁻⁶ peroxidases have been

[†] Laboratoire de Pharmacologie et Toxicologie Fondamentales.

^{††} Laboratoire de Chimie de Coordination.

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