SET and Exciplex Pathways in the Photochemical Reactions between Aromatic Ketones and Benzylsilane and Stannane Derivatives

Laura Cermenati,[†] Mauro Freccero,[‡] Paolo Venturello,[†] and Angelo Albini*,[†,‡]

Contribution from the Istituto di Chimica Organica, Università, I-10125 Torino, and Dipartimento di Chimica Organica, Università, I-27100 Pavia, Italy

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Abstract: The photochemical reaction of α,α,α-trifluoroacetophenone (TFA), benzophenone, and *p*-cyanoacetophenone with benzyltrimethylsilane in MeCN involves hydrogen transfer from the benzylic position. Desilylation occurs as a minor process only in the case of TFA (but it increases greatly in the presence of MeOH or LiClO$_4$). The final products result from the statistical recombination of the benzyl and ketyl radicals. Further cases of intramolecular selectivity studied are *p*-methylbenzyl- and *p*-methoxybenzyltrimethylsilane (the latter substrate undergoes mainly C-Si bond cleavage in the reaction with TFA) as well as benzyltributylstannane (only destannylation observed with all ketones). Product studies are complemented by the determination of relevant kinetic parameters through steady-state and flash-photolysis experiments. The results are explained in terms of hydrogen transfer proceeding from an exciplex and desilylation from the solvent separated radial ion pair. The latter species predominates when $\Delta G_{et} < -10$ kcal mol^{-1}.

Hydrogen atom abstraction by triplet ketones is probably the most extensively investigated photochemical reaction.[1-3] This is rationalized as occurring through either of the two mechanisms, direct homolytic atom transfer or a two-step reaction, viz. electron transfer followed by proton transfer. The latter mechanism has been first proposed for amines and has been since firmly established for that case[2,4] but appears to have a role also with weaker donors such as alkylbenzenes.[5] Thus, a series of papers by Wagner et al. on the photochemical reaction between aromatic ketones and alkylbenzenes, including rate constant determinations, isotope effects, and product selectivity with *p*-cymene, led to the conclusion that an intermediate CT complex is involved although "full" electron transfer does not take place, and the degree of charge transfer occurring affects both the rate of complex formation and of hydrogen transfer within the complex.

In the meantime the scope of electron transfer in organic chemistry has been considerably widened, and a large amount of data on photoinduced single electron transfer (SET) reactions between benzylic donors and acceptors such as aromatic nitriles and heterocycles and their reactivity has accumulated;[6] as an example, relative rates of fragmentation of different electrofugal groups (=groups leaving as a cation) from benzylic radical cations have been established.[6e]

The increased knowledge about the chemistry of bona fide radical ion pairs prompted us to study the photochemical reaction of aromatic ketones with benzylic donors containing a second potential electrofugal group besides the proton, in the hope that they could function as a sensitive probe for testing the contribution of a charge transfer path to ketone photoreduction.

Results

The substrates investigated were trifluoroacetophenone (TFA), *p*-cyanoacetophenone (CAP), and benzophenone (BP), three ketones of similar triplet energy (*ca.* 69 kcal mol^{-1})[7] but with different electronic structure (the lowest triplet is a ππ* state in the first two cases, a nπ* in the last one) and reduction potential (see below). Quenchers used were benzyltrimethylsilane and some of its derivatives and benzyltributylstannane.

Product Studies. TFA was reduced when irradiated in acetonitrile in the presence of benzyltrimethylsilane (**1**); chromatographic separation gave the two diastereoisomeric pinacols **2a** and **2′a** (pairs of diastereoisomeric compounds are indicated by primed and unprimed numbers throughout, see Scheme 1 for the structures) as well as three alcohols, the main components being the two diastereoisomeric silylated derivatives **3a** and **3′a** and the minor one the diphenylpropanol **4a**, and four nonhydroxylated compounds, viz. the diastereoisomeric bis(silyl) derivatives **5** and **5′**, the silane **6**, and bibenzyl (**7**) (see Table 1 for products yield). The corresponding reaction of BP and CAP gave a less complicated product distribution. In the case of BP, this included the pinacol **2b**, the silylated alcohol **3b**, and the silanes **5** and **5′**. In the case of CAP products included pairs of diastereoisomeric pinacols (**2c** and **2′c**), alcohols (**3c** and **3′c**), and silanes (**5** and **5′**).

Irradiation in the presence of benzyltributylstannane (**8**) likewise caused the reduction of the three ketones to the corresponding pinacols **2** with concurrent formation of bibenzyl (**7**). Further products were the phenylethanols **4a**, **4b**, and **4c**, respectively, from the three ketones (the last one underwent partial dehydration to triphenylethylene during workup); in the case of CAP, a different product, the ketone **9**, was also formed (Scheme 1, Table 1).

† Torino.

‡ Pavia.

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(1) Wagner, P. J.; Park, B. S. *Org. Photochem.* **1991**, *11*, 227.

(2) Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141.

(3) Formosinho, S. J.; Arnaut, L. G. *Adv. Photochem.* **1991**, *16*, 67.

(4) Griller, D.; Howard, J. A.; Marriot, P. R.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 612.

(5) Wagner, P. J.; Truman, R. J.; Puchalski, H. E.; Wake, R. *J. Am. Chem. Soc.* **1986**, *108*, 7727.

(6) (a) Albini, A.; Sulpizio, A. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Vol. C, p 88. (b) Lablache-Combier, A. in ref 6a, p 134. (c) Mariano, P. S. in ref 6a, p 372. (d) Albini, A.; Fasani, E.; Mella, M. *Top. Curr. Chem.* **1993**, *168*, 143. (e) Saeva, F. D. *Top. Curr. Chem.* **1990**, *156*, 59. (e) d'Alessandro, N.; Albini, A.; Mariano, P. S. *J. Org. Chem.* **1993**, *58*, 937.

(7) Murov, S. L.; Carmichael, I. ; Hug, G. L. *Handbook of Photochemistry*; Dekker: New York, 1993.
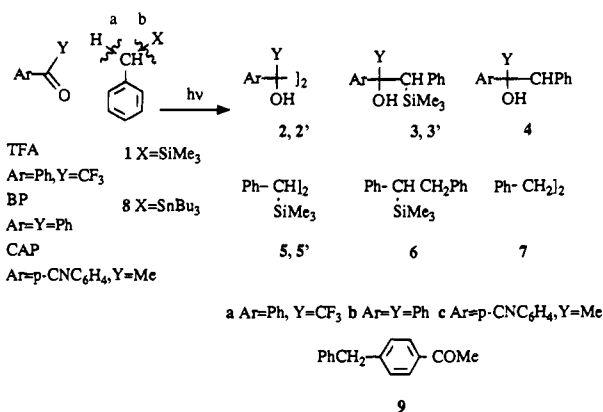
Scheme 1

Scheme 2

Table 1. Results from Preparative Irradiation of Aromatic Ketones in the Presence of the Organometallic Derivatives **1** and **8** and Separation of the Photoproducts by Column Chromatography

do-nor	ke-tone	products (% yield)[a]
1	TFA	2a(9), 2′a(5), 3a + 3′a(20), 4a(tr), 5(8), 5′(6), 6(2) 7(tr)
	BP	2b(15), 3b(35), 5(9), 5′(7)
	CAP	2c + 2c′(18), 3c(9), 3c′(6), 5(2), 5′(2), 6(2)
8	TFA	2a(7), 2′a(4), 4a(59), 7(6)
	BP	2b(14), 3b(35),[b] 7(8)
	CAP	2c + 2c′(24), 3b(36), 7(14), 9(10)

[a] Calculated on the reacted ketone; some of the products have not been separated, and the cumulative yield is given here (see Experimental Section). [b] Yield of **3b** 25%, yield of 1,1,2-triphenylethylene arising form it during chromatography 10%.

Isolated yields after prolonged irradiation were low, and this was in part due to the occurrence of secondary photoreactions. As an example, it was observed in separate experiments that the disilylated bibenzyls **5** and **5′** suffered extensive decomposition upon irradiation, the monosilane **6** being among the products. Furthermore, products containing two benzyl groups, and thus arising form further photochemical benzylation of the primary products, were present among the products obtained by extensive irradiation of the ketones, in particular in the reaction with the stannane **8**.
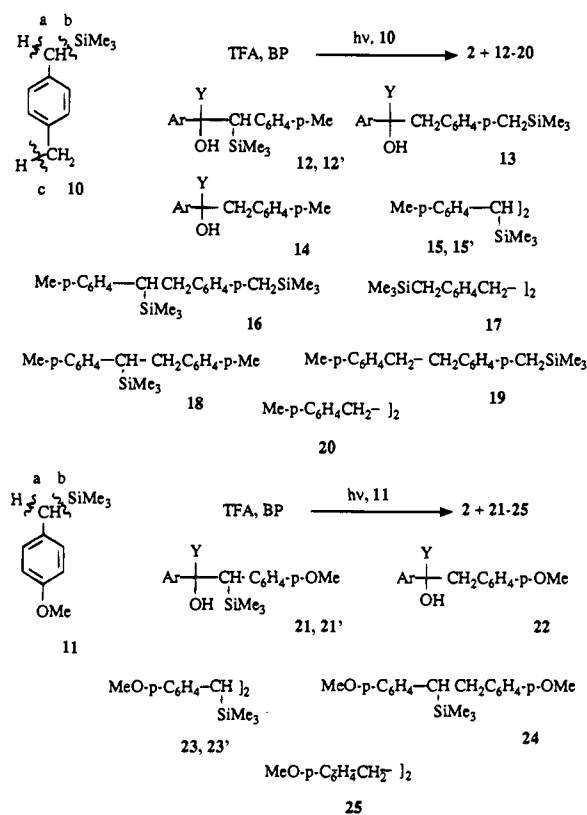
On the other hand, low conversion (ketone converted <20%) experiments with gas-chromatographic detection (see Table 2) showed that at this stage ca. 90% of the reagents consumed was well accounted for by the above reported photoproducts (**2**−**7** and **9**). Furthermore, it also appeared that the ratio between the pinacols **2**, the sum of the (silylated or nonsilylated) alcohols **3** and **4**, and the sum of the bibenzyls **5**, **6**, and **7** was very near to the 1:2:1 ratio expected for a statistical radical recombination of ketyl and benzyl radicals, i.e., the stoichiometry was

4 ketone + 4PhCH₂MMe₃ →

       pinacol + 2 sum of the alcohols +

             sum of the bibenzyls   (M = Si, Sn)
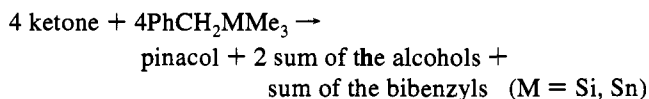
As an examples, in the TFA-1 reaction at 20% conversion of the ketone the gas-chromatographycally determined yields were **2a** + **2′a** (20%), **3a** + **3′a** (42), **4a** (3.5), **5** + **5′**(23), **6**(2), and **7**(tr). This did not hold for the CAP-**8** reaction, where a further type of product was present.

The product distribution was measured under these condition, and since the determination of the silylated and nonsilylated bibenzyls **5**−**7** was particularly easy and accurate, the yields of these products are reported in Table 2, grouping them in three categories, disilylated, monosilylated, and nonsilylated deriva-

tives, and the cleavage ratios used in the mechanistic discussion presented below are based on the yield of these products (we note explicitly, however, that the ratios obtained from the yields of the alcohols are identical within the error limit).

Substituent Effect. The reactivity of TFA and BP was explored also with some derivatives of **1**, viz. *p*-methylbenzylsilane (**10**) and *p*-methoxybenzylsilane (**11**) (Scheme 2). As expected, the product distribution was quite complex. Satisfactory preparative separation of the individual components of the photolysate was not achieved, both because of the large number of products and because of secondary photoreactions occurring in high conversion runs. However, NMR and GC-MS examination of the fractions obtained from low conversion experiments allowed structure attribution to all major products. These were again the pinacols **2** as well as alcohols and bibenzyl derivatives. From **10** the alcohols were the two diastereoisomers **12** and **12′** as well as **13** and **14**; the bibenzyls included the disilylated derivatives **15**, **15′**, **16**, and **17**, the monosilanes **18** and **19**, and a non-silicon containing product **20**. From **11**, the alcohols were **21**, **21′**, and **22**, and the bibenzyls were **23**, **23′**, **24**, and **25** (Scheme 2, Table 2).

Medium Effect. The influence of the medium was tested for the TFA-**1** reaction. As it appears from Table 3, a large change in quantum yield and in the product distribution occurred in the presence of methanol and lithium salts.

Efficiency of the Process. For the reaction reported above, the quantum yield of formation of the various products was measured in a convenient range of concentration of the donors (see Table 4); in these low conversion runs, the product distribution remained unchanged (within 10%) over the concentration range considered (typically from 5 × 10⁻³ to 1 × 10⁻¹ M). The limiting quantum yield for product formation (Φₗᵢₘ) was evaluated from these data. The measurements were extended also to the reactions of TFA and BP with α,α-d₂-**1**.

Flash Photolysis. Most of the systems above were studied by fast spectroscopy after pulsed laser irradiation of the ketone.

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Table 2. Product Distribution in Low Conversion Experiments

donor	ketone	relative yield (%) of bibenzyls						competitive cleavage[a]		
		disilylated			monosilylated		silicon-free	a	b	c
		5 + 5'			6		7			
1	TFA	92			8		<1	0.96	0.04	
	BP	100					1			
	CAP	100					1			
1-d_2	TFA	89			11		<1	0.945	0.055	
	BP	100						1		
8	TFA						100		1	
	BP						100		1	
	CAP				1		100		1	
		15 + 15'	16	17	18	19	20			
10	TFA	32.5	8	35	15.5	9	<1	0.58	0.12	0.29
	BP	43	11	46				0.53		0.27
		23 + 23'			24		25			
11	TFA	7			38		54	0.26	0.74	
	BP	88			12		<1	0.94	0.06	

[a] Calculated from the yields of the products shown in the first columns by using the binomial coefficients, e.g., when two radicals A and B combine and give products A_2, AB and B_2, the yields of these are proportional to $[A]^2$, $2[A][B]$, $[B]^2$ (see text). The modes of fragmentation (a, b, and c) are shown in Schemes 1 (for **1** and **8**) and 2 (for **10** and **11**).

Table 3. Medium Dependence in the Reaction of TFA and **1**

solvent	Φ^a	(H)/(SiMe3)
MeCN	0.2	96/4
MeCN–MeOH 9:1	0.35	40/60
MeCN–MeOH 4:6	0.25	19/81
MeCN, 0.1 M LiClO4	0.38	39/61

[a] Quantum yield of products formation (stoichiometry of the reaction, see text) in low conversion experiments.

**Table 4.** Kinetic Parameters for the Reaction between Aromatic Ketones and Benzylic Donors

donor	ketone	Φ_{lim}	k_i, $M^{-1}s^{-1}$ $\times 10^7$	$k_r(H)$, $M^{-1}s^{-1}$ $\times 10^7$	$k_r(SiMe_3)$, $M^{-1}s^{-1}$ $\times 10^7$	ΔG_{et} kcal mol^{-1}
1	TFA	0.22	19	2	0.17	−4
	BP	0.125	0.27	0.017		+7
1-d_2	TFA	0.17	14.5(1.3)[a]	1.15(1.7)[a]	0.14	
	BP	0.105	0.22(1.2)[a]	0.011(1.5)[a]		
8	TFA	0.195				−17
	BP	0.19				−6
10	TFA	0.37	230	24.5,[b] 8[c]	10	−9
	BP	0.13	1.5	0.05,[b] 0.015[c]		+2
11	TFA	0.45	2100	125	700	−15
	BP	0.3	24	3.3	0.43	−4

[a] Deuterium isotope effect. [b] For abstraction from the CH_2SiMe_3 group. [c] For abstraction from the CH_3 group.

The rate constants for the quenching of the ketone triplets by the benzyl derivatives were determined in this way and are reported as k_i in Table 4. The values obtained span over four orders of magnitudes, reaching the diffusion controlled value in the quenching of TFA by **11**. No transients were detected except in the TFA-**11** reaction where a new absorption with λ_{max} 500 nm was observed (Figure 1); this corresponded well to the spectrum of the species previously obtained by quenching of biphenyl$^{\bullet+}$ by **11** and attributed to the radical cation **11**$^{\bullet+}$.[9] This transient underwent first order decay, with rate constant 1.7×10^6 s^{-1}. Under our conditions no absorptions corresponding to the TFA radical anion or to the corresponding ketyl

(8) We considered the possibility that the primary products of the reaction may be O-silyl or -stannyl derivatives (although, if it were so, these should have been detected by GC), rather than the alcohols and pinacols that are obtained after chromatographic workup, but, even if it were so, this would not affect the conclusion about the mode of fragmentation, since this is unambigously indicated by the retaining of the carbon–heteroatom bond (or the lack thereof) in the alcohols and in the bibenzyls.

(9) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P.; Mattes, S. L. J. Am. Chem. Soc. **1989**, *111*, 8973.
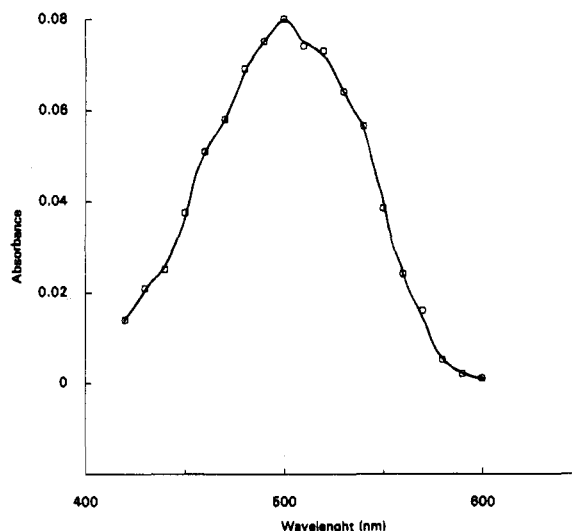

Figure 1. Absorption observed 0.1 μs after flashing a solution of TFA and **11** 1×10^{-4} M.

radical were detected (this may be due to the much lower ε of these species). On the other hand, no transient was detected in the reaction of BP with any of the same donors, including **11**.

Discussion

As stated above, our aim was to obtain information about the mechanism of the ketone photoreaction with benzyl derivatives through the selectivity and efficiency of the fragmentation of a series of silyl and stannyl derivatives, and thus our effort was to get quantitative data on the fragmentation on the basis of product distribution in conjunction with steady state and flash photolysis measurements.

Competitive Fragmentations. In the reactions reported above interaction of triplet excited ketones (for all the cases considered $\Phi_{isc} = 1$) with the benzyl derivatives led to competitive cleavage either of the C–H bond or of the C–Si (or C–Sn) bond with formation respectively of a heteroatom-containing or of a heteroatom-free benzyl radical.

$$ArCH_2^{\bullet} \leftarrow ArCH_2MR_3^{\bullet+} \rightarrow ArCHMR_3^{\bullet} \qquad M = Si, Sn$$
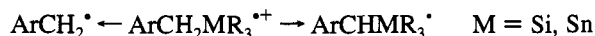
These radicals and the ketone-derived ketyl radicals underwent statistical recombination to yield pinacols, alcohols, and bibenzyls. As mentioned above, the overall yield of isolated

Scheme 3
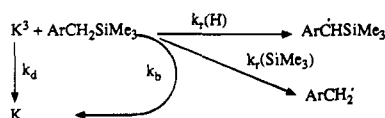
products was not high in preparative experiments, but in low-conversion experiments the material balance of the identified products was good and the ratio between the three different types of products was very near to 1:2:1. Within each one of the categories, the products could be rationalized as arising from the statistical recombination of the radicals formed from the two possible fragmentations (viz. of the C—H or the C-metal bond in the case of **1**, **8**, and **11**, see above; three alternative fragmentations were possible and indeed were recognized to take place from the structure of the final products, in the case of the silane **10**, viz. C—H at the benzylic position, C—Si, and C—H at the methyl group). Thus, the ratio between the different modes of fragmentation could be calculated from the product distribution (as stated above, it was convenient to use the bibenzyls product distribution for this purpose), and the results obtained are reported in the last columns of Table 2 in terms of selectivity of the bond cleavage in the benzyl derivatives (a, b, and c as shown in Schemes 1 and 2).[8]

Rate of Fragmentation. As for the kinetics of the process, the relevant parameters are defined in Scheme 3, the minimal kinetic scheme. The overall rate of quenching of the ketone triplet by the benzyl derivatives, $k_i = k_r + k_b$, was directly measured in flash photolysis experiments. The quenching leads in part to decay to the ground state and in part to chemical reaction. The Φ_{lim} values = fraction of the quenching leading to chemical reaction = $[k_r/(k_r + k_b)]$ was obtained by steady state measurements from the double reciprocal plot of quantum yield vs benzyl derivatives concentration. These data, together with the knowledge of selectivity of the bond cleavage obtained from product distribution (Table 2), allowed the evaluation to be made for the rate at which the quenching process ultimately leads to products via C—H or C—Si bond cleavage in the benzyl derivatives, $k_r = k_i \Phi_{lim}$.

The resulting values are reported in Table 4 as $k_r(H)$ and k_r-(SiMe$_3$), according to which bond is cleaved. In order to take into account the statistical factor when comparing different donors, the observed rate constants were divided by the number of identical CH bonds and thus are expressed as rate constants per single bond cleaved.[10a] These values do not represent the intrinsic rate constants for cleavage of the bonds but are related to them, since the rate of fragmentation determines chemical reaction vs purely physical quenching of triplet ketone, and we used them for checking mechanistic hypothesis, since direct measurements of the cleavage rate constants are unavailable (see above, flash photolysis). Thus, k_i and k_r values are plotted in Figure 2 vs the calculated (Weller equation)[10b,c] free energy change for electron transfer from the benzyl derivatives to the triplet ketones, in order to check whether there is any relation with electron transfer.

Mechanistic Hypotheses. A first general comment which seems appropriate is that several factors differentiate the present photoreactions from the classical model of radical H abstraction.
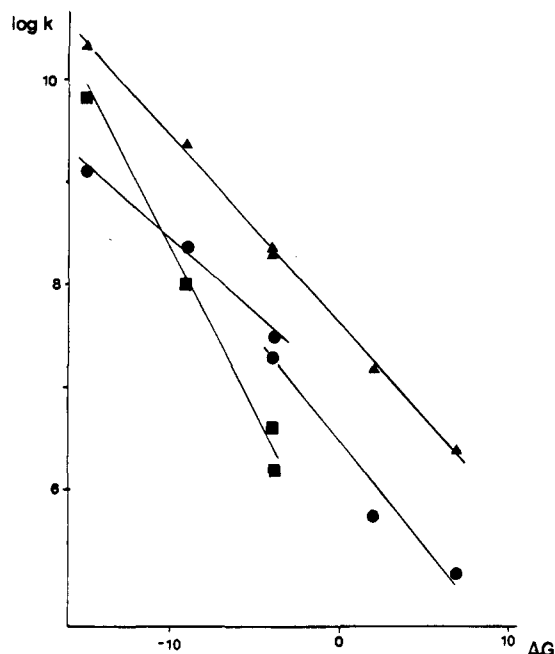

Figure 2. Dependence of k_i (triangles), $k_r(H)$ (circles, right side, with BP; left side, with TFA), and $k_r(SiMe_3)$ (squares) on ΔG_{et}.

Thus, quenching of the ketone triplet is much more efficient than expected for H abstraction, exhibits little isotope effect (see Table 4; the effect is somewhat larger on $k_r(H)$ than on k_i), and is not exclusive of nπ^* states (actually quenching of the $\pi\pi^*$ TFA[3]* is somewhat faster than for BP). Hydrogen transfer cannot be the main mechanism of triplet ketone quenching; furthermore, there is some factor leading to inefficiency, so that in every case decay to the ground state predominates over chemical reaction ($\Phi_{lim} \ll 0.5$). Similar observations for the photoreduction of the same ketones by toluene and cumene led Wagner[5] to propose that a charge transfer mechanism, and not hydrogen abstraction, was operating. However, in his case ΔG_{et} was generally positive, and, since electron transfer was not compatible with the observed rate constants, his model was based on an excited CT complex with only partial but variable charge separation, with the easiest to reduce ketones reacting by irreversible, rate-determining complexation with the alkylbenzenes, and the harder to reduce ketones reacting reversibly, with the hydrogen-transfer step wholly or partially rate determining depending on the extent of the electron transfer in the complex. This model suffers perhaps of some ambiguity, since one has to define the process either as a SET initiated reaction involving full electron transfer where the radical ions undergo the observed chemical reactions or an exciplex process involving complexation of the excited state rather than SET.

For this purpose, the presently considered substrates should be a good choice, since they are better donors, and ΔG_{et} spans over a 25 kcal mol^{-1} range from positive to negative values. Actually, we observe that k_i varies rather regularly with ΔG_{et} over >3 orders of magnitude, and so does $k_r(H)$, while $k_r(SiMe_3)$ sets in only at negative ΔG_{et} values but grows more steeply over 4 orders of magnitude.

Appropriateness of the Model Chosen. We set out this investigation with the aim of establishing whether the competition between the C—H and C-heteroatom cleavages could tell something about the electron transfer nature of the photochemical process, and thus should first check whether the model is appropriate. For this purpose, one can attempt to evaluate the relevant thermodynamics on one hand and review the known experimental studies on the other.

(10) (a) This is strictly appropriate only if it is assumed that the protons remain equivalent during the reaction; it would not be appropriate if only a particular conformation reacts. Statistical corrections introduce no relevant change in the correlation with ΔG_{et} (Figure 2), but we felt it more appropriate to consider them explicitly. (b) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (c) $E_{red}(BP)$ −1.83 V vs SCE, $E_{red}(CAP)$ −1.58 V, $E_{red}(TFA)$ −1.38 V, see ref 5. Oxidation potential of the donors, see ref 11.

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The free energy change for the competitive fragmentations of $1^{\cdot+}$ (eqs 1 and 2) can be evaluated through the appropriate

$$PhCH_2SiMe_3^{\cdot+} \rightarrow PhCHSiMe_3^{\cdot} + H^+ \qquad (1)$$

$$PhCH_2SiMe_3^{\cdot+} \rightarrow PhCH_2^{\cdot} + SiMe_3^+ \qquad (2)$$

thermochemical cycle as shown in eqs 3 and 4, where $\Delta G(C-H)$ or $(C-Si)$ represents the bond dissociation energy in the radical cation, $BDE(C-H)$ or $(C-Si)$ the corresponding quantity in the neutral substrate, and E_{ox} the oxidation potential of the indicated species.[12]

$$\Delta G(C-H) = BDE(C-H) - [E_{ox}(1) - E_{ox}(H)] \qquad (3)$$

$$\Delta G(C-Si) = BDE(C-Si) - [E_{ox}(1) - E_{ox}(SiMe_3^{\cdot})] \qquad (4)$$

In the case of deprotonation of $1^{\cdot+}$, all required data are available, and one calculates that the process is exothermic (ΔG ca. -9 kcal mol^{-1}).[12] In the case of desilylation, the answer is less simple, since $E_{ox}(SiMe_3^{\cdot})$ is not known. If instead of this quantity one uses the IP value obtained from the appearance potential of $SiMe_3^+$ in the mass spectrum,[12] the reaction results largely endothermic (by ca. 30 kcal mol^{-1}). The ΔG_{et} for $11^{\cdot+}$ are higher by 10 kcal mol^{-1} than the analogous values for $1^{\cdot+}$, due to the lower E_{ox} of the methoxy derivative,[11] thus ca. 0 for eq 1 and ca. 40 kcal^{-1} mol^{-1} for eq 2. Previously, Dinnocenzo et al. had remarked that desilylation of $1^{\cdot+}$ is fast despite the fact that the process involves a high barrier, as calculated above, and proposed that actually a nucleophile assisted process is involved (eq 5).[9]

$$PhCH_2SiMe_3^{\cdot+} + Nu \rightarrow PhCH_2^{\cdot} + NuSiMe_3^+ \qquad (5)$$

We feel that the above evaluation is inappropriate, since it assumes that solvation does not contribute differently to the energy of the starting radical cation and the resulting cation.[13] At any rate, whatever the mechanism may be, flash photolysis experiments show that desilylation of $1^{\cdot+}$ is very fast in MeCN (k_r ca. 10^9 s^{-1})[9] and is also fast with $11^{\cdot+}$ (k_r 2.3×10^6 s^{-1} in ref 9, 1.8×10^6 in this work). As for destannylation, even when the gas phase appearance potential is used, a reduced barrier (ca. 15 kcal mol^{-1}) is obtained,[14] and the process can be safely assumed to be very fast in acetonitrile.

Previous product studies carried out in various laboratories consistently showed that desilylation is always the exclusive process from benzylsilanes when electron transfer, both photoinduced and thermal, is involved.[15–18] In particular, it is instructive to compare the present results with those obtained with the same donors and aromatic nitriles[15] or imides[16] as the acceptors, where it was found that desilylation is always preferred to deprotonation. Studies based on the intramolecular competition in the photoreaction of *p*-xylene derivatives with 1,4-naphthalenedicarbonitrile (DCN) showed that in benzylic radical cations $k_r(H) < 10^{-2}k_r(SiMe_3)$.[6e] It has also been shown that

desilylation of **1** photoinduced by DCN remains equally effective in MeCN, MeCN−MeOH, and MeCN−MeOH in the presence of KOH.[17]

Thus, it appears safe to assume that deprotonation of $1^{\cdot+}$ and related radical cations, although exothermic, is a slow process, and desilylation, which involves a small barrier, is always the kinetically preferred path from solvated radical cations.

Exciplex vs SET Mechanism. In rationalizing the present results, one has to define clearly the intermediates involved. Important suggestions come from previous literature. Thus, Peters et al. found[19] that in the BP^{3*}−dimethylaniline system (electron transfer largely exothermic) a solvent separated ion radical pair (SSIRP) is first formed, and it decays in 300 ps to the contact ion radical pair (CIRP), where proton transfer takes place with rate 2×10^9 s^{-1} (3×10^8 s^{-1} per hydrogen atom). Polar protic solvents and alkali perchlorates stabilize the SSIRP.[20] Furthermore, Mariano found[21,22] that in the photoreaction between unsaturated ketones and α-silylamines (electron transfer again exothermic) deprotonation dominates in MeCN (as well as in apolar solvents) and desilylation dominates in the presence of alcohols or lithium salts. This result is explained by considering that the ketone radical anion is a strong base (while the radical anions of quinones, imides or arenenitriles are less basic and only desilylation is observed) and induces selective proton transfer, unless H-bonding or Li$^+$ complexation control its nucleophilicity.

Suggested Mechanism. We feel that the photochemical reaction between ketones and benzylsilanes is best explained

(13) (a) While it may be true that solvation contributes equally to reagents and products when both species have a similar structure, this is hardly expected to be the case for the reaction of eq 2, where the strongly localized σ SiMe$_3$+ cation is formed from the delocalized π radical cation $1^{\cdot+}$. Nothing definitive is known about solvation energies of such species; however, Wayner has calculated that the solvation energy of benzylic *cations* in acetonitrile is 10−15 kcal mol^{-1} lower than that of more localized carbocations, e.g., $\Delta G_{solv}(PhCH_2^+) = -39.3$ kcal mol^{-1}, while for the more localized $CH_3OCH_2^+$ cation $\Delta G_{solv} = -56$ kcal mol^{-1}, ref 13b. The value for a strongly localized σ cation ion such as Me_3Si^+ is expected to be larger, and thus the difference in solvation energy beween $1^{\cdot+}$ and Me_3Si^+, $\Delta\Delta G_{solv}$, is probably ca. 20 kcal mol^{-1} for the process depicted in eq 2. Thus, we expect that a more realistic evaluation for $\Delta G(C-Si)$ in $1^{\cdot+}$ is around 10 kcal mol^{-1}.[13] On the other hand, one may understand the role of MeCN as that of a nucleophile rather than generically that of a polar solvent: acetonitrile is sufficiently nucleophilic to assist the desilylation (eq 6, a particular application of eq 5) and silylated acetonitrile is formed (just as is the case for MeCNH$^+$ in the case of deprotonation).

$$PhCH_2SiMe_3^{\cdot+} + MeCN \rightarrow PhCH_2^{\cdot} + MeC\!\!=\!\!NSiMe_3^+ \qquad (6)$$
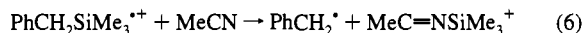
We think that the barrier for desilylation for $1^{\cdot+}$ is low, for the reasons suggested above. However, we do not exclude that it may be high in other cases. Thus, the radical cations of some sterically hindered *p*-methoxybenzylalkylsilanes cleave more slowly than $11^{\cdot+}$, and the reaction is accelerated by a nucleophile better than MeCN, such as an alcohol.[9] This does point to nucleophile assisted desilylation in those cases. (b) Wayner, D. D. M.; Sim, B. A.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56*, 4853.

(14) $E_{ox}(15)$ 0.85 vs Ag/Ag$^+$, BDE (C−Sn) 45 kcal mol^{-1}, see: Cottrell, T. L. *The Strength of the Chemical Bond*; Butterworths: London, 1954

(15) Albini, A.; Fasani, E.; Mella, M. *Top. Curr. Chem.* **1993**, *168*, 143.

(16) Freccero, M.; Fasani, E.; Albini, A. *J. Org. Chem.* **1993**, *58*, 1740.

(17) Fasani, E.; d'Alessandro, N.; Albini, A.; Mariano, P. A. *J. Org. Chem.* **1994**, *59*, 829.

(18) (a) Baciocchi, E.; Bernini, R.; Lanzalunga, O. *J. Chem. Soc., Chem. Commun.* **1993**, 1691. (b) Baciocchi, E.; Del Giacco, T.; Rol, C.; Sebastiani, G. V. *Tetrahedron Lett.* **1989**, 3573. (c) Sirimanne, S. R.; Li, Z.; Vender Veer, D. R.; Tolbert, L. M. *J. Am. Chem. Soc.* **1991**, *113*, 1766. (d) Baciocchi, E.; Crescenzi, M.; Fasella, E.; Mattioli, M. *J. Org. Chem.* **1992**, *57*, 4684.

(19) (a) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6403. (b) Manring, L. E.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 6452.

(20) (a) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1982**, *104*, 6542. (b) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 4875.

(21) (a) Yoon, U. C.; Kim, J. U.; Hasegawa, E.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 4421. (b) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *J. Am. Chem. Soc.* **1988**, *110*, 8099.

(22) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **1982**, *25*, 233.

(11) (a) $E_{ox}(1)$ 1.78 V vs SCE, $E_{ox}(10)$ 1.57V, $E_{ox}(11)$ 1.31 V, refs 9 and 12b. (b) Koizumi, T.; Fuchugama, T.; Nonaka, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 219.

(12) (a) For benzyltrimethylsilane: BDE(C−H) 77 kcal mol^{-1}, BDE-(C−Si) 75 kcal mol^{-1}, $E_{ox}(H)$ −1.77 V (vs NHE, ref 12b). Since $E_{ox}(SiMe_3)$ has not been measured, the value for desilylation is taken from ref 9, where gas phase values are used, IP(1) 8.35 V, IP(SiMe$_3$) 148 kcal M^{-1}, obtained from the measured AP(SiMe$_3^+$) from mass spectroscopy, ref 12c. (b) Parker, V. D. *J. Am. Chem. Soc.* **1993**, *115*, 1201. (c) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 2085.
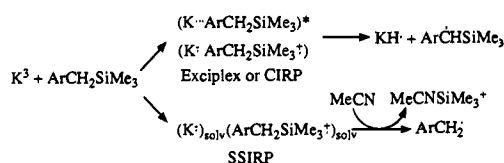
Scheme 4

through two mechanisms. Comparison of the results of the chemical reactions reported in Table 2 and of the free energy data reported in Table 3 shows that desilylation occurs in neat MeCN only when full electron transfer is feasible and becomes dominant only for $\Delta G_{et} < -12$ kcal mol^{-1}, viz. in the TFA-**11** reaction. In that case, flash-photolysis reveals the formation of the solvated radical cation, and thus desilylation occurs from the SSIRP (see Scheme 4). The same process occurs also at less negative ΔG_{et} values, but then only under conditions favoring separation and solvation of the radical ions such as addition of methanol or salts (see Table 3). Likewise, when the carbon—heteroatom bond is weaker, C—Sn rather than C—Si as with **8**, demetalation becomes exclusive (see Table 2). Thus, cleavage of the carbon—heteroatom bond is the diagnostic reaction for the free radical cation with these benzyl derivatives.

On the other hand, deprotonation and not desilylation takes place as ΔG_{et} approaches zero. This contrasts with what is observed with other acceptors. Indeed, desilylation remains the exclusive process with arenenitriles and phthalimides;[15,16] with the latter compounds it has been demonstrated that only desilylation takes place both with ΔG_{et} near to thermoneutral and with negative ΔG_{et}.[16] Thus, deprotonation is a specific reaction of the ketones. As Figure 2 shows, the deprotonation *rate* constant continues to grows with decreasing ΔG_{et}, although at markedly negative values an increasingly important *fraction* of the reaction is diverted to desilylation from the SSIRP. Furthermore, when the rate constants for deprotonation measured by Wagner with alkylbenzenes[5] are considered in conjunction with those presently obtained with benzylsilanes, it turns out that k_i and k_r(H) both increase steadily over more than four orders of magnitude from ΔG_{et} +20 to −15 kcal mol^{-1} finally reaching the same value observed for proton transfer in the PhNMe$_2$−BP reaction (see above).

The continuity between the positive and negative ΔG_{et} zones suggests that the same mechanism is operating in both cases. Two intermediates can be considered: the exciplex and the CIRP (Scheme 4). Indeed, we would expect similar properties for both species. The exciplex, according to the classical definition, is described by a mixture of wave functions relative to both charged and noncharged structures:[23]

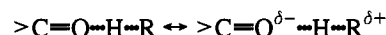$$\psi(A^*D) \leftrightarrow \psi(A^{\bullet-}D^{\bullet+})$$
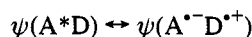
Now, it has been shown that even in typical cases of hydrogen abstraction by BP the reaction occurs via an early transition state, and that its rate is correlated with the ionization potential of the *radical* formed.[24a] This is relevant to the present case, since at least with delocalized π radicals like the benzyl radicals used here, the ionization potential of the radicals will change

in the same way, although less steeply than, as that of the starting molecules. Thus, even if a hydrogen transfer mechanism would operate, k_r(H) is expected to increase roughly proportionally to the decrease of ΔG_{et}.[24b] In other words, the more polar is the transition state, the faster is hydrogen transfer

$$>C=O\cdots H\cdots R \leftrightarrow >C=O^{\delta-}\cdots H\cdots R^{\delta+}$$

and this holds even when ΔG_{et} remains positive, since exciplex formation causes mutual polarization of the two substrates (reasonably proportionally to ΔG_{et}).[24b]

On the other hand, if the CIRP is the intermediate, one must take into account that the radical anion of ketones are, as mentioned above, good nucleophiles (e.g., in the case of BP$^{\bullet-}$, the pKa of the the corresponding ketyl radical in water is 9.2;[25ab] in contrast, other radical anions, e.g., those of aromatic nitriles,[25c,d] are weak bases). Thus, with ketones in cage proton transfer is expected to be very fast in the CIRP.
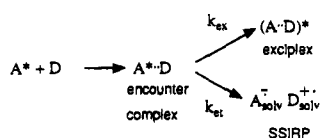
Thus, it may be that the difference between an exciplex and a CIRP, at least in this case, is purely semantic. A useful piece of evidence is the intramolecular regioselectivity observed in the deprotonation of **10**, which can be rationalized as due to the polarization of the exciplex. Thus, the CH$_2$ vs CH$_3$ H abstraction ratio from **10** is 2:1 with both BP and TFA. This is reminiscent of the preference for Me vs *i*-Pr H abstraction observed by Wagner with *p*-cymene (which grows with increasing charge transfer contribution)[5] and can similarly be attributed to the preferred conformation for the exciplex being that where the positive and negative sites of the donor/acceptor polarized pair are opposed. In the case of *p*-cymene, the methyl group better stabilizes the positive charge and so does the CH$_2$SiMe$_3$ group in the case of **10** (with the additional advantage that the large silyl group is pushed far from the acceptor by sterical hindrance in the complex, and this brings the C−H bond in the suitable position for H transfer to the carbonyl). Orientation effects have been observed also in the BP-aniline reaction,[19] which, as mentioned before, has been attributed to the CIRP but is certainly equally appropriate for an exciplex, and the similarity observed in the reaction course in the positive and negative ΔG_{et} regions supports the identification of the exciplex as the intermediate.

The deprotonation rate is little dependent on the structure of the ketone triplet. If the data relative to the $\pi\pi^*$ TFA triplet and those relative to the $n\pi^*$ BP triplet are separately considered, small differences in the extrapolated rate constants result (Figure 2). Wagner previously found[5] that TFA and BP react in a parallel but a quantitatively different way with alkylbenzenes, and he attributed this effect to the fact that $n\pi^*$ and $\pi\pi^*$ states form charge transfer complexes of different geometries. This may apply here too, although the effect is in both cases rather small.
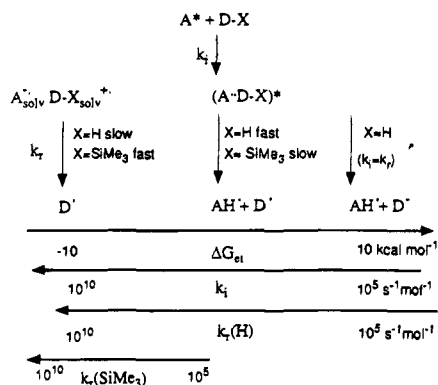
Summing up, demetalation is the characteristic reaction of the solvated radical cation of benzylsilanes and stannanes, independent on the nature of the acceptor, while deprotonation is an in-cage process typical of ketones; thus, overall reaction rate constants, such as the k_r determined in this work, reflect the environment in which the fragmentation occurs. Triplet ketone induced proton transfer occurs via an exciplex, which may come to coincide with the CIRP under conditions where SET occurs, although there is no need to invoke a different intermediate in that case, at least judging from the observed

(23) (a) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 839. (b) Stevens, B. *Adv. Photochem.* **1971**, *8*, 161. (c) Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45.

(24) Naguib, Y. M. A.; Steel, C.; Cohen, S. G.; Young, M. A. *J. Phys. Chem.* **1987**, *91*, 3033. (b) The effect of the ionization potential of the radical formed on the hydrogen abstraction rate is probably enhanced with more easily reduced ketones. Hence, it is possible that the correlation of the (likewise indirectly determined) rate constants of ketone—alkylbenzenes reactions with the ketone E_{red} observed by Wagner can be discussed in the same terms. This would explain while the slope observed is lower than expected for "full" electron transfer.

(25) Hayon, E.; Ibata, J.; Lichtin, N. N.; Simic, M. *J. Phys. Chem.* **1972**, *76*, 2072. (b) Beckett, A.; Porter, G. *Trans. Faraday Soc.* **1961**, *37*, 1686. (c) Kellet, M. A.; Whitten, D. G.; Gould, I. R.; Bergmark, W. R. *J. Am. Chem. Soc.* **1991**, *113*, 358. (d) Freccero, M.; Mella, M.; Albini, A. *Tetrahedron* **1994**, *50*, 2155.

SET and Exciplex Pathways in Photochemical Reactions

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Scheme 5

$$A^* + D \longrightarrow A^* \cdots D \underset{k_{et}}{\overset{k_{ex}}{\rightrightarrows}} \begin{array}{l} (A \cdot D)^* \text{ exciplex} \\ A^-_{solv} D^+_{solv} \text{ SSIRP} \end{array}$$

encounter complex

Scheme 6

$$A^* + D\text{-}X$$

$k_i \downarrow$

$A^-_{solv} D\text{-}X^+_{solv}$ $(A \cdots D\text{-}X)^*$

k_r | X=H slow, X=SiMe$_3$ fast   X=H fast, X=SiMe$_3$ slow   X=H (k_i=k_r)

$D^{\cdot}$ $AH^{\cdot} + D^{\cdot}$ $AH^{\cdot} + D^{\cdot}$

	ΔG_{et}	
-10		10 kcal mol^{-1}
10^{10}	k_i	10^5 s^{-1} mol^{-1}
10^{10}	k_r(H)	10^5 s^{-1} mol^{-1}
10^{10}	k_r(SiMe$_3$)	10^5

chemistry. The fact that an exciplex reaction occurs even for moderately exothermic electron transfer and the SSIRP reactivity takes in only at $\Delta G_{et} < -10$ kcal mol^{-1} has a parallel in the photocycloaddition of aromatics with alkenes[26] and dienes,[27] where two different exciplexes are involved for positive and near thermoneutral electron transfer, while the radical ion chemistry sets in at markedly negative ΔG_{et}. After this work had been finished, we found further support to the exciplex—SSIRP model we propose here in the work of other groups. Thus, Gould, Farid, and co-workers published a detailed study[28] of the fluorescence of arenenitriles in the presence of aromatic donors and found that SSIRP and exciplexes are formed from two competitive paths from the initial encounter complex (Scheme 5, with $k_{ex} = k_{et}$ with ΔG_{et} ca. -10 kcal mol^{-1}). Furthermore, Baciocchi and co-workers found[29] that in the reaction between chloranil and **1** desilylation is the exclusive process in MeCN, but deprotonation occurs in benzene, where the CIRP, or the exciplex, is supposed to predominate.

Conclusions. In summary, the picture we gather from these results and previous literature involves three mechanisms for hydrogen transfer to excited ketones (or at least vinyl and aryl ketones, Scheme 6). (1) With poor donors the reaction occurs according to the classical homolytic, radical abstraction; it occurs from nπ^* states only and shows $k_i = k_r$(H) [however, nπ^* triplets behave as electrophyllic radicals, and k_r(H) depends on E_{ox}-(D$^{\cdot}$)].[24] (2) With moderate donors an exciplex is formed; the observed values of both k_i and k_r are larger than in the previous case and depend on E_{ox}(DH) growing over several orders of magnitude in a roughly parallel way, while the charge transfer character of the exciplex increases; $k_i > k_r$(H) and the limiting quantum yield is less than unit, contrary to case 1; the nature of the ketone triplet has little effect; stereoelectronic effects are important in determining selectivities. At negative ΔG_{et} values the intermediate may become the CIRP, but, if it is so, this shows the same chemistry as the exciplex, and it is not necessary to postulate such an intermediate with benzylic donors. (3) With good donors ($\Delta G_{et} < -10$ kcal mol^{-1}) the SSIRP is formed at a diffusion controlled rate; the free benzylic radical cation

probably does not deprotonate at a rate sufficient to compete with back electron transfer and thus an inefficient reaction results (indeed also with the anilines proton transfer occurs from the CIRP, not the SSIRP); however, when a better electrofugal group, such as the silyl cation, is present, fragmentation occurs at the free ions stage, revealing the mechanism. Notice that with still better donors (and thus strongly stabilized free radical cations), such as α-silylalkylanilines, *both* deprotonation and desilylation from the SSIRP (generated with a non-nucleophilic acceptor) are slow and are only induced by a nucleophile (or silophile) induced second order process, as recently shown by Mariano and co-workers.[30] This last one may be considered as case 4. Pending a study on the picosecond, or lower, time scale, which may reveal the evolution of exciplexes and SSIRP, at the moment we were unable to determine the detailed sequence of events, e.g., whether the different intermediates are formed from a common precursor or sequentially, but we could attribute the different *reactions* observed to *specific intermediates*.

Although the mechanism we have summarized here, or at least several aspects of it, may be said to have been already presented in previous literature, we feel that the presently reported desilylation—deprotonation competition makes the chemical characterization of the intermediates more explicit.

Experimental Section

α,α-d_2-Benzyltrimethylsilane. α,α-d_2-Benzyl alcohol (6.6 g, 54 mmol)[31] was added dropwise in 1 h to the solution obtained from 10.1 mL of 37% HCl and 17.1 g anhydrous ZnCl$_2$ at -5 °C. The solution was allowed to reach room temperature and after 3 h was extracted with 3 × 20 mL of diethyl ether. Distillation yielded 5.4 g (77% yield, bp 78—80 °C, 20 mmHg) of the chloride. The corresponding Grignard derivative was prepared by reaction with 1.09 g of magnesium turnings in 40 mL of diethyl ether. Me$_3$SiCl (10.6 mL) in 20 mL of Et$_2$O was added dropwise, and the solution was refluxed for 3 h. Usual workup and distillation (bp 90—92 °C, 20 mmHg) gave the title product (3.85 g, 55% yield).

Preparative Irradiations. A solution of TFA (0.19 g, 11 mmol) and benzyltrimethylsilane (**1**, 0.5 g, 30 mmol) in 200 mL pf acetonitrile was deaerated by flushing with argon and then irradiated for 2 h in an immersion well apparatus by means of a 150 W Italquartz high pressure mercury arc through a Pyrex filter while maintaining a slow stream of argon. The solvent was evaporated under reduced pressure, and the residue chromatographed on silica gel (Merk 60) eluting with light petroleum ether—diethyl ether mixtures of increasing polarity. The following products were obtained: unreacted TFA (90 mg); meso-1,2-diphenyl-1,2-bis-(trimethylsilyl)ethane (**5**, 7.5 mg, 8% on converted TFA, mp 156—157 °C from methanol, lit.[32] 155—156 °C); DL isomer of **5** (**5'**, 5.5 mg, 6%, mp 53—54 °C from heptane, lit.[32] 50—52 °C); 1,2-(diphenylethyl)trimethylsilane (**6**, 1.5 mg, 2%, oil);[33] meso-1,1,1,4,4,4-hexafluoro-2,3-diphenylbutandiol (**2a**, 9 mg, 9%, mp 157—158 °C from heptane, lit.[34] 155—156 °C); (DL) isomer of **2a** (**2a'**, 5 mg, 5%, oil); mixture of diastereoisomeric 1,1,1-trifluoro-2,3-diphenyl-3-(trimethylsilyl)propan-2-ol (**3a** + **3a'**, 19.5 mg, 20%, oil); 1,1,1-

(26) Mattay, J. *Tetrahedron* **1985**, *41*, 2393 and 2405.

(27) Albini, A.; Fasani, E.; Giavarini, F. *J. Org. Chem.* **1988**, *53*, 5601.

(28) Gould, I. R.; Young, R. H.; Mueller, L. J.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8176.

(29) Baciocchi, E. personal communication. We thank Professor Baciocchi for communicating his results previous to publication.

(30) Zhang, X.; Yeh, S.; Hong, S.; Freccero, M.; Albini, A.; Falvey, D.; Mariano, P. S. *J. Am. Chem. Soc.* **1994**, *116*, 4211.

(31) Buncel, E. C.; Bourns, A. N. *Can. J. Chem.* **1960**, *38*, 2457.

(32) Huang, H. H. *Aust. J. Chem.* **1976**, *29*, 2415.

(33) West, J. D. *J. Org. Chem.* **1980**, *45*, 3120.

(34) Mosher, W. A.; Heindel, N. D. *J. Am. Chem. Soc.* **1963**, *85*, 1548.

trifluoro-2,3-diphenylpropan-2-ol (**4a**, detected by GC, isolated in the TFA-**8** reaction, see below).

3a + 3a′: ^{1}H NMR (in CDCl$_3$) (major isomer) δ −0.3 (s, 9H), 3.0 (s, 1H), 3.1 (s, 1H, OH), 7.15−7.5 (m, 8H), 7.7 (d, $J = 8$ Hz, 2H); (minor isomer) δ −0.6 (s, 9H), 2.8 (s, 1H, OH), 2.95 (s, 1H, CH), 7.15−7.5 (m, 8H), 7.7 (d, $J = 8$ Hz, 2H); ^{13}C NMR (major isomer) δ −0.6 (Me), 44.5 (CH), 80.0 (C-OH), 126 (CF$_3$); (minor isomer) δ 0.1 (Me), 44.2 (CH), 80.4 (C-OH), 126.5 (CF$_3$) IR 3550, 1150, 835 cm^{-1}. Anal. Calcd for C$_{18}$H$_{21}$F$_3$OSi: C, 63.88; H, 6.25. Found: C, 63.8; H, 6.25.

4a: ^{1}H NMR (in CDCl$_3$) δ 2.6 (s, 1H, OH), 3.5 (AB q, 2H), 7.0 (m, 2H), 7.25 (m, 3H), 7.4 (m, 3H), 7.55 (m, 2H); IR 3540, 1150 cm^{-1}. Anal. Calcd for C$_{15}$H$_{13}$F$_3$OSi: C, 67.66; H, 4.92. Found: C, 67.4; H, 5.0.

5: ^{1}H NMR (in CDCl$_3$) δ −0.05 (s, 9H), 3.0 (s, 1H), 7.4 (s, 5H); IR 1660, 1240, 835 cm^{-1}. Anal. Calcd for C$_{20}$H$_{30}$Si$_2$: C, 73.55; H, 9.26. Found: C, 73.2; H, 9.4.

5′: ^{1}H NMR (in CDCl$_3$) δ 0.0 (s, 9H), 3.0 (s, 1H), 7.3−7.4 (m, 5H); IR 1660, 1240, 835 cm^{-1}. Anal. Found: C, 67.8; H, 5.1.

6: ^{1}H NMR (in CDCl$_3$) δ 0.0 (s, 9H), 2.4 (t, $J = 8$Hz, 1H), 3.9 (d, 2H), 7.0−7.4 (m, 10H); IR 1600, 1240, 835 cm^{-1}. Anal Calcd for C$_{17}$H$_{22}$Si: C, 80.25; H, 8.72. Found: C, 80.1; H, 8.6.

The reaction of TFA, BP, and CAP with the silane **1** and the stannane **8** were carried out analogously, as detailed in Table 1. Some of the products had been previously reported (**2b**, **4b**,^{5} and **9**).^{35} The following new products were isolated.

3b: ^{1}H NMR (in CDCl$_3$) δ −0.05 (s, 9H), 2.9 (s, 1H), 3.8 (s, 1H, OH), 7.0−7.5 (m, 15H); IR 3580, 855, 835 cm^{-1}; mp 117−121 °C (MeOH). Anal. Calcd for C$_{23}$H$_{26}$OSi: C, 79.72; H, 7.56. Found: 79.5; H, 7.7. 1,1,3-Triphenylethene, presumably arising from the dehydration of **3b** during chromatography was also isolated.

2c + 2c′:^{36} ^{1}H NMR (in CD$_3$COCD$_3$) (major isomer) δ 1.75 (s, 3H) 2.5 (s, 1H, OH), 7.48 (ABq, 4H); (minor isomer) δ 1.5 (s, 3H), 2.2 (s, 1H, OH), 7.7 (ABq, 4H); ^{13}C NMR (in CD$_3$COCD$_3$) (major isomer) δ 24.2, 77.9, 110.1, 116.9 (CN), 126.4, 130.4, 151.6; (minor isomer) δ 24.6, 77.6, 110.3, 116.9 (CN), 126.9, 130.6, 151.7; IR 3460, 2220, 1100 cm^{-1}; mp 219−42 °C (MeOH). Anal. Calcd for C$_{18}$H$_{16}$N$_2$: C, 83.04; H, 6.20; N, 10.76. Found: C, 82.8; H, 6.2; N, 10.6.

3c: ^{1}H NMR; δ 0.05 (s, 9H), 0.4 (s, 1H), 1.6 (s, 3H), 2.75 (s, 1H, OH), 7.5 (m, 7H), 7.8 (m, 2H); IR 3500, 2220, 1070, 840 cm^{-1}; mp (MeOH) 137−138 °C. Anal. Calcd for C$_{19}$H$_{23}$NOSi: C, 73.68; H, 7.49; N, 4.53. Found: C, 73.6; H, 7.6; 1, 4.4.

3c′: ^{1}H NMR (in CDCl$_3$) δ 0.1 (s, 9H), 0.5 (s, 1H), 1.8 (s, 3H), 2.65 (s, 1H, OH), 7−7.4 (m, 9H); IR 3470, 2220, 1105, 835 cm^{-1}; mp 159−162 °C (MeOH). Anal. Found: C, 73.6; H, 7.6; N, 4.4.

4c: ^{1}H NMR (in CDCl$_3$) δ 1.5 (s, 3H), 2.25 (s, 1H, OH), 3.0 (s, 2H), 6.8−7.3 (ABq, 4H), 7.4 (s, 5H); IR 3670, 2220, 790 cm^{-1}; mp 72−74 °C (MeOH). Anal. Calcd for C$_{16}$H$_{15}$NO: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.0; H, 6.5; N. 5.7.

As for the reaction with the silanes **10** and **11**, preparative separation was unsatisfactory, due to the complex product distribution and the intervening of further processes at high conversion. Thus, product identification was mainly based on gas chromatographic separation and mass spectrometric data (peak with intensity >10% or less when significant for interpretation and m/z > 100 reported) from low conversion experiments.

12a: m/z 262 (100, M − Me$_3$SiOH), 247 (28), 227 (22), 225 (12), 193 (55), 178 (27), 149 (21), 105 (44).

12a′: m/z 262 (100), 247 (27), 227 (15), 225 (11), 223 (13), 193 (50), 178 (23), 105 (53).

12b: 342 (12, M − H$_2$O), 327 (11), 271 (23), 270 (100), 255 (35), 254 (11), 253 (11), 183 (37), 178 (16), 135 (12), 105 (50), 73 (44). The corresponding alkene, [2,2-diphenyl-1-(4-methylphenyl)ethenyl]-trimethylsilane [m/z 342 (23, M)] was also identified.

13a: m/z 352 (9, M), 193 (11), 177 (74), 105 (24).

13b: m/z 342 (60, M − H$_2$O), 270 (1), 255 (21), 183 (64), 178 (25), 105 (57), 73 (100). The corresponding alkene, 1-phenyl-2-(trimethylsilylmethylphenyl)ethene [m/z 342 (12, M)] also identified.

14a: m/z 280 (2, M), 279 (7), 175 (5), 106 (43), 105 (100).

15: m/z 356 (1, M), 354 (13), 281 (25), 177 (4), 149 (8), 73 (100).

15′: m/z 354 (5), 281 (10), 177 (1), 149 (5), 73 (100).

16: m/z 354 (5), 281 (3), 280 (11), 236 (24), 177 (18), 149 (18), 148 (24), 73 (100).

17: m/z 356 (2), 354 (25), 178 (10), 177 (55), 148 (1), 73 (100).

18: m/z 282 (17), 208 (64), 193 (14), 178 (10), 149 (34), 118 (68), 73 (100).

19: m/z 282 (5), 280 (12), 178 (5), 177 (31), 73 (100).

20: m/z 210 (21, M), 105 (100).

21a: m/z 280 (1, M − SiMe$_3$OH), 279 (13), 278 (100), 209 (11), 165 (13), 105 (11).

21a′: m/z 368 (1, M), 279 (14), 278 (100), 209 (13), 165 (14), 105 (16).

21b: m/z 358 (16, M − H$_2$O), 343 (13), 287 (16), 286 (100), 194 (16), 183 (32), 179 (16), 135 (13), 105 (50). The corresponding alkene, [2,2-diphenyl-1-(4′-methoxyphenyl)ethyl]trimethylsilane (m/z 358, 20, M) was also identified.

22a: m/z 296 (12, M), 122 (37), 121 (100), 105 (24).

22b: m/z 304 (9, M), 286 (12), 122 (35), 121 (100).

23: m/z 386 (2, M), 371 (24), 356 (13), 298 (20), 283 (13), 193 (10), 165 (22), 73 (100).

23′: m/z 386 (10), 372 (24), 371 (69), 313 (15), 299 (13), 298 (53), 283 (29), 240 (12), 73 (100).

24: 314 (19, M), 300 (21), 299 (100), 193 (29).

25: 242 (37, M), 122 (24), 121 (100).

Quantum Yield Determination. Absolute quantum yields were determined on 3 mL of a solution of the acceptor (5×10^{-2} M) and the donor in spectrophotometric cuvettes after degassing by five freeze−thaw−degas cycles. These were irradiated by means of a focalized Osram 150-W high-pressure mercury arc fitted with an interference filter centered at 313 nm. For actinometry, a potassium trioxaloferrate (III) solution was used. The product formation was monitored by GC using dodecane as the internal standard.

Laser Flash Photolysis. These experiments were performed with either of the two sources: (1) a Questek 2120 excimer laser using a XeCl reagent gas which provides UV pulses at 308 nm with a duration of 6−10 ns and pulse energy of 30−50 mJ (for TFA) or (2) a Q-switched Nd-YAG laser (Model HY 200 JK Laser Ltd. Lumonics), which provided pulses at 355 nm (third harmonic) with a duration of 8 ns and pulse energy of 30 mJ (for BP). A Hamamatzu R 928 photomultiplier was the detector. We thank Dr F. Elisei, Perugia, Italy, for assistance during the excimer laser experiments.

(35) Nakai, Y.; Takabayashi, T.; Yamada, F. *Org. Magn. Reson.* **1980**, *13*, 94.

(36) Clerici, A.; Porta, O. *J. Org. Chem.* **1985**, *50*, 76.