Tetrahedron Vol. 39, No. 7, pp 1109 to 1111, 1983
Printed in Great Britain.

0040-4020/83/071109-03$03.00/0

THE PHOTOCHEMISTRY OF *o*-[(TRIMETHYLSILYL)METHYL]ACETOPHENONE

WILLIAM R. BERGMARK,* MICHAEL MEADOR, JAMES ISAACS and MICHAEL THIIM
Department of Chemistry, Ithaca College, Ithaca, NY 14850, U.S.A.

(*Received in USA* 2 *April* 1982)

Abstract—The title compound was prepared and irradiated under a variety of conditions to produce no change. Irradiation in DMSO-d_6 and methanol-d_4 results in D incorporation into the *o*-(trimethylsilyl)methyl group. Irradiation in 2-propanol results in photoreduction ($\phi = 0.012$) which could be quenched with dienes ($k_q\tau = 4.5$). These results are taken to suggest a rapid, efficient, and reversible H- transfer with no detectable silyl transfer.

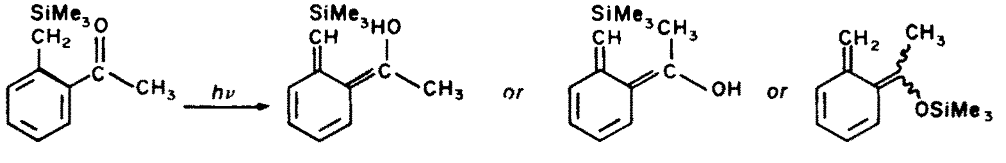
Hydrogen abstraction by n, π^* excited CO groups is a particularly common photochemical reaction. We wondered if this photochemical sigmatropic rearrangement was limited to H- transfer. For a number of reasons we considered the trimethylsilyl group as an attractive possibility for such a transfer: the Si–O bond has a high bond energy and there is a well-known preference for Si–O bonds over Si–C;[1] furthermore, silyl transfer is known to occur in mass spectromety in the so-called silyl-McLafferty rearrangement.[2] The similarity of the McLafferty rearrangement and the Type II photoreaction has often been referred to.[3]

Aryl ketones with *ortho* Me groups are noteworthy for their very rapid and efficient H-transfer, a process termed photoenolization.[4,5] The efficiency is due, in large measure, to the favorable, fixed geometry. On this basis we looked for silyl transfer in *o*-[(trimethylsilyl)methyl]-acetophenone, **1**. The trimethylsilyl group could be introduced synthetically by treatment of the dianion of *o*-toluic acid with chlorotrimethylsilane. The silated acid could then be converted to the ketone **1**. Irradiation of **1** under a variety of conditions produced no observable chemical change. Attempts to trap photoenol **2** or photoenol ether **3** using dienophiles, deuterated solvents, or O_2 under conditions known to be effective in trapping other related structures[4] also resulted in no observable reaction. The only successful trapping experiment utilized a procedure of Wirz and Wagner[5] in which D was incorporated into the *o*-methylene group on irradiation in a solvent mixture of dimethylsulfoxide-d_6 and methanol-d_4 with a quantum efficiency that was 90% of that of *o*-methylacetophenone under the same conditions. The process could be partially quenched (about 50%) by addition of 1 M 2,5-dimethyl-2,4-hexadiene.

In general, when photoenols are trapped in Diels–Alder reaction the product stereochemistry indicates that only the (*E*)-isomer, e.g. **2**-(*E*), is trapped. Because of its very rapid reversion to ketone the (*Z*)-photoenols are too short-lived to be trapped except for the method of Wirz and Wagner. This fact or the posibility that they are not formed to a significant extent must explain the observed stereoselectivity. Since no Diels–Alder trapping is observed in the case of **1**, this suggests that **2**-(*E*) is not forming in detectable amounts, or is not sufficiently reactive.

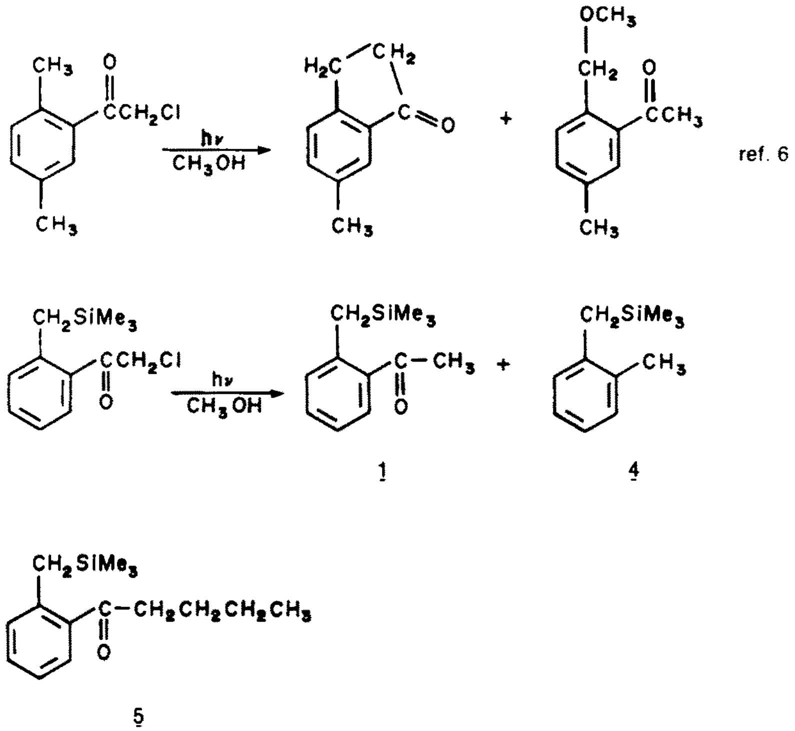
Another approach to capturing photoenol intermediates involves internal cyclization or nucleophilic displacement as is illustrated in the top equation of Scheme 2.[6] The second equation indicates that inclusion of the trimethylsilyl group in the *o*-Me completely alters the photochemistry. The products observed, **1** and **4**, are characteristic of the photochemistry of some phenacyl chlorides without *o*-Me groups.[7] The simplest rationalization for these observations is the formation of phenacyl radical from loss of a Cl atom, followed by H-abstraction or rearrangement, (aryl migration), decarbonylation and then H- abstraction from solvent. These results suggest either the absence of photoenolization or an ineffective partitioning of photoenol to products vs starting material.

Experiments were undertaken to characterize the excited state involved in these processes. Irradiation of **1** in 2-propanol resulted in photoreduction (pinacol form tion). This process was quite inefficient, quantum yield = 0.012. The inefficient photoreduction could be quenched with 2,5-dimethyl-2,4-hexadiene. A normal linear Stern-Volmer plot was obtained, the slope of which indicated a very short triplet lifetime: $k_q\tau = 4.5$. If quenching is near diffusion control, that indicates a lifetime of about 1 ns. A short triplet lifetime is also indicated by the low



1 2-(Z) 2-(E) 3-(E or Z)

Scheme 1.



Scheme 2.

quantum yield for the Type II photoreaction, $\phi = 0.004$, for o-[trimethyl(silyl)-methyl]valerophenone, 5. Here the competing H-abstraction is intramolecular. Complete analysis of this quantum yield would require knowledge of the distribution of rotational isomers in the excited state.[8] Nonetheless, it seems safe to conclude that a rapid photoenolization is competing withe the Type II reaction.

In summary, these results taken together suggest to us the following events: Compound 1 undergoes an efficient, rapid and reversible H atom transfer with no detectable silyl transfer (formation of 3). The results of the trapping experiments indicate that the initially formed biradical does not extensively form the (*E*)-dienol, a conclusion consistent with the results from the corresponding chloroketone.

EXPERIMENTAL

All solvents used were of reagent or spectral quality. THF was distilled over LAH and used promptly after distillation. t-BuOH was distilled over Na.

^{1}H-NMR spectra were recorded on a Varian T-60 spectrometer. IR spectra were recorded on a Perkin–Elmer 337 IR Spectrophotometer. UV spectra were recorded on a Cary 14 Recording Spectrophotometer. Gas chromatography was performed on a Perkin–Elmer 900 or Varian 1700 Gas Chromatograph using a 6′ 3% SE-30 column. Photochemical reactions were performed using a Rayonet Photochemical Reactor equipped with 3000 Å lamps and quartz photolysis tubes. For all reactions, except O_2 trapping experiments, the samples were flushed with N_2. Quantum yield data were obtained with a merry-go-round device.

o-[(*Trimethylsilyl*)*methyl*]*benzoic acid*. A soln of o-toluic acid (20.0 g, 0.147 mmole) in 50 mL of THF (anhyd) was added to a stirred soln of lithium diisopropyl amide (0.294 mmole, prepared by the addition of 108.7 mL of a 2.7 M soln of n-BuLi in hexanes to 41.2 mL diisopropylamine (0.294 mmole) in 50 mL of anhyd THF) under a N_2 with vigorous stirring. The resulting dianion of o-toluic acid (deep red in color) was quenched by a dropwise addition of chlorotrimethylsilane (distilled under N_2, 18.6 mL, 146.8 mmole). The soln was allowed to stir for 15 min and then poured over 400 mL water. Extraction with ether (3 × 100 mL) removed the neutral material (e.g. o-silylated products). The aqueous layer was then acidified and extracted with ether (2 × 125 mL). The ether extracts were dried ($MgSO_4$) and the ether evaporated. The crude acid was immediately converted to its corresponding acid chloride.

o-[(*Trimethylsilyl*)*methyl*]*benzoyl chloride*. $SOCl_2$ (11.0 mL, 0.147 mmole) was added to a soln of crude o-[(trimethylsilyl)methyl]-benzoic acid from above and DMF (0.5 mL) in benzene (250 mL). The soln was refluxed for 6 hr and the benzene evaporated. The resulting dark liquid was vacuum distilled to give o-[(trimethylsilyl)methyl]benzoyl chloride (13.4 g, 40% overall yield from o-toluic acid). b.p. (1 mm Hg) 88–90°; ^{1}H-NMR (CCl_4) $\delta = 0.0$ ppm (s, 9H); 2.62 (s, 2H); 7.0–8.0 (m, 4H). (Found: C, 57.99; H, 6.67. Calcd. for $C_{11}H_{15}ClOSi$: C, 58.26; H, 6.66).

o-[(*Trimethylsilyl*)*methyl*]*acetophenone*, 1. A soln of MeMgI (22.4 mmole, prepared from MeI (1.40 mL, 22.4 mmole) and Mg filings (0.54 g, 22.4 mmole) in 25 mL anhyd diethyl ether) was added under N_2 to a stirred soln of o-[(trimethylsilyl)methyl]benzoyl chloride (4.80 g, 20.4 mmole) in 20 mL anhyd ether at −25°. The resulting soln was extracted with water (2 × 100 ml), the ether extract dried ($MgSO_4$), and the ether evaporated. The resulting dark liquid was vacuum distilled to yield the pure 1 (1.8 g, 43% yield). bp (1 mm Hg) 90–93°; ^{1}H NMR (CCl_4) $\delta = 0.0$ ppm (s, 9H), -Si$(CH_3)_3$; 2.3 ppm (s, 3H), 2.4 ppm (s, 2H), 6.9–7.9 ppm (m, 4H). IR (film) cm^{-1} 1680 (s). uv (2-propanol) λ_{max} 300 nm, ϵ 2260; λ_{max} 248 nm, ϵ 7710. (Found: C, 69.82; H, 9.00. Calc for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79).

o-[(*Trimethylsilyl*)*methyl*]*valerophenone*, 5, was prepared by adding lithium dibutylcuprate (13.4 mmole, prepared under N_2 by adding n-BuLi, 26.6 mmole, to a stirred suspension of cuprous bromide, 1.90 g, 13.4 mmole, in 20 mL anhyd ether) to a stirred soln of o-[(trimethylsilyl)methyl]benzoyl chloride (3.1 g, 13.7 mmole) in 30 mL anhyd ether at −5°. The soln was allowed to warm to room temp and extracted with a sat $NaHCO_3$aq and dried ($MgSO_4$). After evaporation the residue was distilled to give 5, 1.5 g (45%), bp 109–110° (2 mm). NMR (CCl_4) δ 0.00 (s, 9H), 0.75–1.90 (m, 7H), 2.50 (s, 2H), 2.81 (t, 2H), 6.8–7.6 (m, 4H). (Found C, 72.41, H, 9.91. Calc for $C_{15}H_{24}OSi$: C, 72.58; H, 9.68) H, 9.91.

α-Chloro-o-[(trimethylsilyl)methyl]acetophenone was prepared by adding t-butyl hypochlorite (0.87 g, 7.40 mmole) to a stirred soln of 1 (1.62 g, 7.40 mmole) and a catalytic amount of *p*-toluenesulfonic acid, 5 mg, in 10 mL CCl_4. The soln was refluxed for 3 hr, washed with a 5% NaOH aq (2 × 50 mL), and dried ($MgSO_4$). After removal of the solvent, the crude *α*-chloro-*o*-[(trimethylsilyl)methyl]- acetophenone was purified for use in the preparative GLC. NMR (CCl_4) δ 0.00 (s, 9H), 2.62 (s, 2H), 4.45 (s, 2H), 7.02–7.84 (m, 4H). UV (hexanes): λ_{max} 304 nm, ϵ 3210; λ_{max} 253 nm, ϵ 9680; λ_{max} 248 nm, ϵ 9540 (shoulder). (*Found*: C, 60.02; H, 7.02. Calc for $C_{12}H_{17}OSiCl$: C, 59.85; H, 7.02).

Photolysis of o-*[(trimethylsilyl)methyl]valerophenone.* Two photolysis tubes were charged with 2.0 mL solns of *o*-[(trimethylsilyl)methyl]valerophenone in t-BuOH (1.12×10^{-4} M and 1.37×10^{-4} M, respectively. Hexadecane (60 mg) was added to each sample. A 2.0 mL soln of valerophenone in benzene (1.0×10^{-2} M) was used as an actinometer. After irradiation for *ca.* 20 hr the solns were analyzed via GLC for the loss of valerophenone. The sole product was identified as 1.

Photolysis of 1. A soln of 30 mg 1 in 250 μL of a 50% mixture of MeOH-d_4 and DmSO-d_6 was irradiated in a N_2 bubbled, sealed NMR tube in parellel with an equimolar soln of *o*-methylacetophenone. Loss of signal from the *ortho* positions was monitored by NMR.

The photoreduction of 1 in 2-propanol was monitored by the disappearance of the n, π^* absorption band of 1 at λ_{max} = 300 nm. The irradiation was carried out with a 8.86×10^{-3} M soln of 1 in quartz tubes with various amonts of 2,5-dimethyl-2,4-hexadiene.

*Photolysis of α-chloro-*o*-[(trimethylsilyl)methyl]acetophenone*, **6**, A photolysis tube, charged with 10 mL of a soln of **6** in hexanes (1.09×10^{-2} M) was irradiated for *ca.* 22 hr. The solvent was evaporated and the residue separated by preparative GLC which indicated only two major fractions. The two fractions collected were analyzed *via* IR and ^1H NMR (90 MHz, Varian EM-390) and found to be *o*-[(trimethylsilyl)methyl]acetophenone and *o*-[(trimethyl)silyl]-toluene and formed in a 2:1 ratio. ^1H NMR *o*-[(trimethylsilyl)methyl]acetophenone same as described before; *o*-[-trimethylsilyl)methyl]toluene: $\delta = 0.0$ ppm (s, 9H); 2.5 (s, 3H); 2.55 (s, 2H); 7.0–8.0 (m, 4H).

Acknowledgement—The authors wish to thank the Research Corporation for their support of this work and Prof. David Evans for a discussion which initiated this study.

REFERENCES

[1] L. H. Sommer, *Stereochemistry, Mechanism and Silicon*, p. 25ff. McGraw-Hill, New York (1965); C. Eaborn, *Organosilicon Compounds*, p. 90. Butterworth, London (1960).
[2] W. P. Weber, R. A. Felix and A. K. Willard, *J. Am. Chem. Soc.* **92**, 1420 (1970).
[3] H. Budzikiewicz, C. Djerassi and D. H. Williams, *Mass Spectrometry of Organic Compounds*. Holden-Day, San Francisco (1967).
[4] P. G. Sammes, *Tetrahedron* **32**, 405 (1976).
[5] R. Haag, J. Wirz and P. J. Wagner, *Helv. Chim. Acta* **60**, 2595 (1977).
[6] W. R. Bergmark, *Chem. Commun.* 61 (1978).
[7] J. C. Anderson and C. B. Reese, *Tetrahedron Letters* 1 (1962); H. E. Zimmerman, *Adv. Photochem.* **1**, 199 (1963).
[8] P. J. Wagner and C. -P. Chen, *J. Am. Chem. Soc.* **98**, 239 (1976).