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ELECTRON TRANSFER - INDUCED PHOTOCHEMICAL REACTIONS IN IMIDE - $RXCH_2TMS$ SYSTEMS. PHOTOADDITION OF α - TRIMETHYLSILYL SUBSTITUTED HETEROATOM CONTAINING COMPOUNDS TO PHTHALIMIDES

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Abstract —— Studies have been conducted to explore single electron transfer (SET) induced photoaddition reactions of phthalimides with the α-silyl-n-electron donors ($EtOCH_2TMS$, $n\text{-}PrSCH_2TMS$ and Et_2NCH_2TMS). Photoadditions of $EtOCH_2TMS$, $n\text{-}PrSCH_2TMS$ and Et_2NCH_2TMS to phthalimides in CH_3CN or CH_3OH occur in moderate to high yields to produce 3 - substituted phthalimidines.

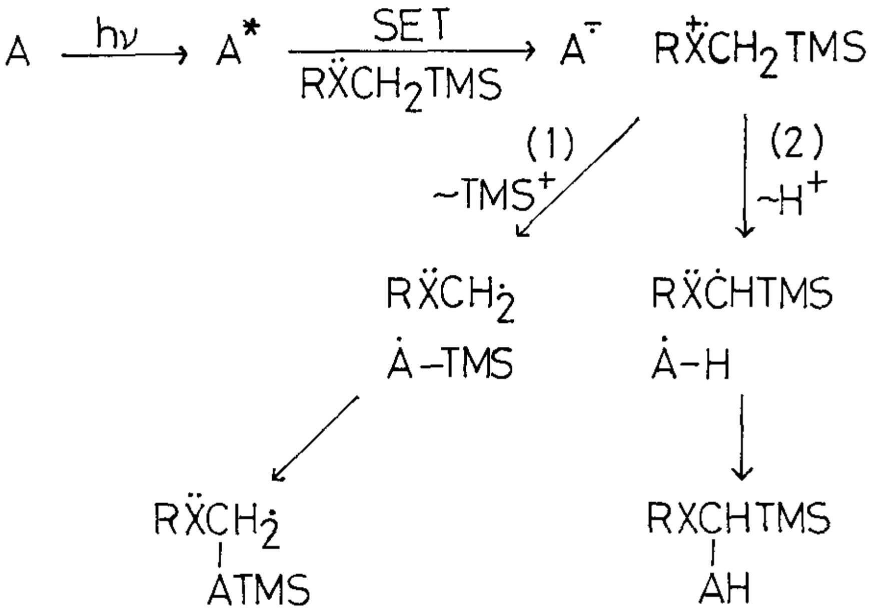
The primary photoadducts undergo dehydration (or desilanolation) to generate 3-alkylidenylphthalimidine derivatives by pathways which are accelerated by acid impurity.

Mechanisms for these photoadditions involving SET from α-silyl-n-electron donors to excited phthalimides followed by selective desilylation of the intermediate cation redicals and radical coupling are proposed.

Previously we demonstrated how photochemical processes operating via single electron transfer(SET) of α-trimethylsilyl substituted electron donors can be employed to generate free radical systems.[1] Initial efforts focused on SET processes of iminium salts.[1] Recently, we expanded this methodology to include arenecarbonitriles[2] and cyclohexenones.[3] Product formation in these

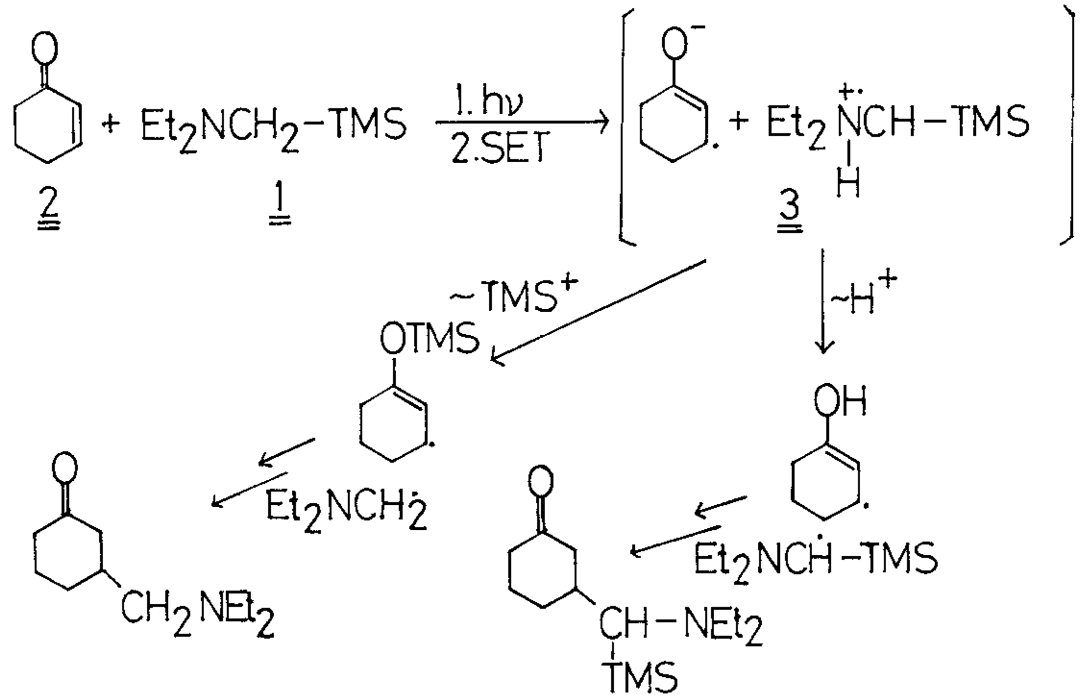
SET reactions is often governed by unique secondary processes of the initially formed ion radicals (Scheme 1) involving transfer of electrofugal groups (trimethylsilyl (TMS) group (path 1) or proton (H^+) (path 2)) from donor cation to acceptor anion radicals. Cation radicals generated by photoinduced SET from α-trimethylsilyl substituted donors are known to undergo preferential desilylation to produce neutral, non-silicon containing radicals (path 1), even when competitive deprotonation pathways are available (path 2).

Scheme 1.



Observations which support this conclusion have come from efforts probing the SET photochemistry of allylsilane,[1a,1b] benzylsilane,[1c,4] α-silyl ether, and α-silyl thioether systems.[1d,2] These observations suggest that sequential SET-desilylation pathways have the potential of serving as efficient and highly regioselective methods for making α-alkoxy-, α-alkylthio-, and α-amino substituted carbon radicals. In contrast to this are observations made in a recent investigation of the photoinduced SET chemistry of the α-silylamine, Et_2NCH_2TMS(1) with cyclohexenone (2) which have demonstrated[3] that a competition exists between reaction pathways formally involving α-deprotonation and desilylation of the intermediate amine cation radical 3 (Scheme 2). The relative efficiencies of these competitive pathways appear to be governed by factors which influence the nature (contact ion pairs vs. free ions) of reactive ion radical intermediates.

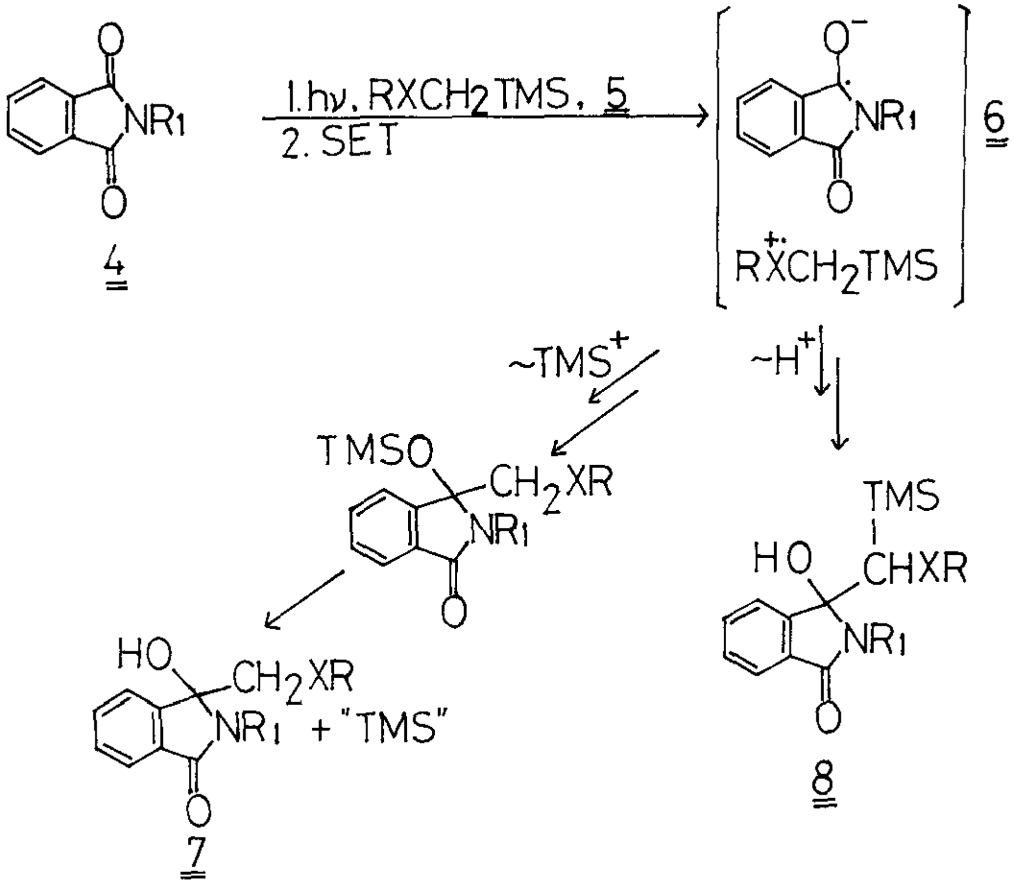
Scheme 2.



Earlier studies[5] have shown that N-substituted phthalimides serve as excited state electron acceptors in photochemical reactions with donors such as alkenes, tertiary amines, ethers and thioethers. Furthermore, SET-induced photochemical cyclization of N-substituted phthalimides can be used in the synthesis of heterocyclic compounds.[6] However the SET-induced photochemical reactions of N-substituted phthalimides often lead to non-regioselective cyclization producing regioisomeric mixtures when more than one type of α-proton is bonded to carbons adjacent to heteroatom electron donor site. An example of this is found in the photocyclization of thioalkyl-phthalimide.[6b]

Our observations[1d,2] using α-trimethylsilyl substituted donors in photoinduced SET reactions and earlier studies of the photochemical reactions of N-substituted phthalimides combine to suggest that a highly efficient and regioselective method for phthalimide-$RXCH_2TMS$ photoaddition is possible. Stimulated by this possibility and guided by a long range goal to develop synthetically useful photoinduced SET reactions, we have investigated photoaddition reactions of phthalimides with α-trimethylsilyl substituted heteroatom compounds. In this study, we also were interested in examining whether a competition exists between reaction pathways involving sequential SET-deprotonation and SET-desilylation (Scheme 3). Accordingly we anticipated that photoaddition of α-trimethylsilyl

Scheme 3.



substituted heteroatom compounds, RXCH$_2$TMS (5) to phthalimides (4) would follow SET mechanisms, that two kinds of adducts might be generated via proton or TMS group transfer in the intermediate radical ion pair(6), and that partitioning between these pathways might be controlled by medium effects which govern the nature of intermediate ion radical pairs.

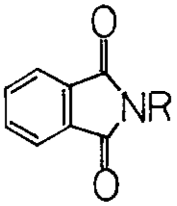
RESULTS

α-Silyl Ether, α-Silyl Thioether, and α-Silylamine Photoadditions to Phthalimide and Its N-Methyl Derivative.

Photoaddition reactions of phthalimides (4a, b) and the α-silyl substituted heteroatom compounds, (trimethylsilylmethyl ethyl ether (9), trimethylsilylmethyl n-propyl thioether (10) and N-trimethylsilylmethyl-N, N-diethylamine (11) were explored. Preparative reactions were conducted by irradiation of CH_3CN or CH_3OH solutions of the phthalimides (ca. 7mM-14mM) and α-silyl substituted compounds 9-11 (ca. 20-60mM) by using a Pyrex filtered-light (>290nm). The nature of products generated and the gross chemical efficiencies were evaluated for these processes which were conducted at phthalimide conversions ranging from 50% to 95%. Product separations employed silica gel chromatographic methods (Experimental Section). Product distributions and yields along with reaction conditions used are recorded in Table 1. The adducts produced in these reactions appear to be generated via pathways involving sequential SET-desilylation. Structural assignments to photoadducts were made on the basis of characteristic spectroscopic data (Experimental Section). Ir spectra of photoadducts 12, 13, 15, 16, and 21 contain characteristic bands for hydroxy group at 3,100-3,650 cm^{-1} and carbonyl group at 1,600-1,680 cm^{-1}. Their ^{1}H-nmr and ^{13}C-nmr spectra clearly show resonances which correspond to the respective diethylaminomethyl-, ethoxymethyl- and n-propylthiomethyl groups. In addition resonances for tertiary carbons (C-3) at 88-90 ppm are prominent in the ^{13}C-nmr spectra of these substances. All of the spectral features including high resolution mass spectrum are in complete accord with the structures assigned.

Elimination of Photoadducts to Olefinic Products.

In addition to alcohol type photoaddition products, olefin products were present



4a (R=Me)

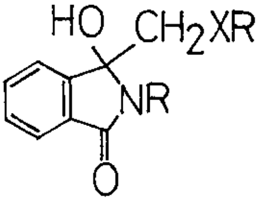
4b (R=H)

TMSCH$_2$-$\ddot{X}$-R

9 (X-R=OEt)

10 (X-R=S-n-Pr)

11 (X-R=NEt$_2$)



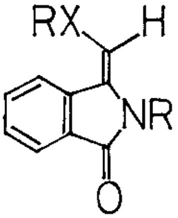
12 (R=Me, XR=OEt)

13 (R=H, XR=OEt)

15 (R=Me, XR=S-n-Pr)

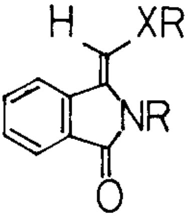
16 (R=H, XR=S-n-Pr)

21 (R=Me, XR=NEt$_2$)



17 (R=Me, XR=S-n-Pr)

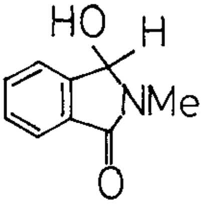
18 (R=H, XR=S-n-Pr)



14 (R=H, XR=OEt)

19 (R=Me, XR=S-n-Pr)

20 (R=H, XR=S-n-Pr)



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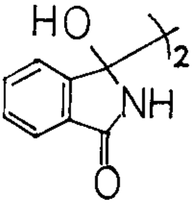

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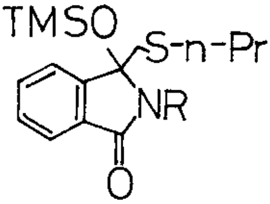


24a (R=Me)

24b (R=H)

Table 1. Photochemical Reactions between Phthalimides 4a, b and α-Silyl Substituted Heteroatom Compounds 9 - 11

Phthalimide	$RXCH_2TMS$	(Phthalimide) / ($RXCH_2TMS$)	Solvent	Reaction time (h)	Conversion of 4	Products (yield)[a]
4a	9	12mM / 60mM	CH_3OH	4	62	12(40%)
4a	9	12mM / 60mM	CH_3CN	13	48	12(27%)
4b	9	14mM / 40mM	CH_3OH	2	47	13(12%),14(36%)
4b	9	14mM / 40mM	CH_3CN			no reaction
4a	10	9mM / 45mM	CH_3OH	1	75	15(78%)
4a	10	9mM / 45mM	CH_3CN	2	48	15(78%),17(26%) 19(46%)
4b	10	11mM / 22mM	CH_3OH	0.7	79	16(85%)
4b	10	11mM / 22mM	CH_3CN	2	13	16(47%),18(16%) 20(34%)
4a	11	9mM / 27mM	CH_3OH	2	86	22(33%)
4a	11	9mM / 27mM	CH_3CN	2	97	21(41%),22(22%)
4a	11	9mM / 27mM	CH_2Cl_2	2	52	21(20%),22(30%)
4a	11	7mM / 21mM	hexane	1.5	55	22(83%)
4b	11	8mM / 23mM	CH_3OH or CH_3CN	2	95	23(75%)

(a) Yields are based upon consumed phthalimide.

in the mixtures obtained from photoreaction of phthalimides with α-silyl thioether 10 in CH_3CN. The products 17 and 19, and 18 and 20 appear to be formed by secondary dark processes involving desilanolation of initially formed photoadducts 24a, b or dehydration of photoadducts 15 and 16 respectively. Spectroscopic data for these olefinic products are consistent with structures assigned. Especially characteristic are resonances in the ^1H-nmr spectra for the olefinic hydrogens at 5.2-6.2 ppm. The positions of these resonances suggest the stereochemistry of the geometric isomers 17 and 19, and 18 and 20.

Accordingly, proton chemical shifts of **17** (5.7 ppm) and **19** (5.9 ppm), and those for **18** (6.10 ppm) and **20** (6.19 ppm) allow assignments of **19** and **20** as Z-isomers and **17** and **18** as E-isomers. This follows from the expectation that aromatic ring anisotropic effects in **19** and **20** should operate to shift the olefinic proton resonances downfield. The stereochemical assignments are also supported by the observation that yields of **19** and **20** are from 1.5 to 2 times higher than **17** and **18**. The pure olefin isomers undergo slow isomerization to produce equilibrium mixtures of the corresponding E- and Z-isomers at ambient temperatures. The isomerizations are accelerated by the addition of trace quantities of acids. Thus, diastereomeric ratios **17**:**19** and **18**:**20**, appear to reflect thermodynamics with the least sterically encumbered isomers **19** and **20** (lacking thioalkyl-ortho aryl hydrogen interactions) predominating. Although two geometric isomers of **14** are thought to be also generated by dehydration of the initially formed photoadduct **13** in photoreaction of phthalimide (**4b**) with α-silyl ether **9**, only one major isomer was isolated. This was assigned as the Z-isomer of **14**. No attempt was made to locate the E-isomer of **14** which would have been present in only trace quantity.

Photochemical Reaction of Phthalimide with α-Silyl Thioether in the Presence of Acid and Base.

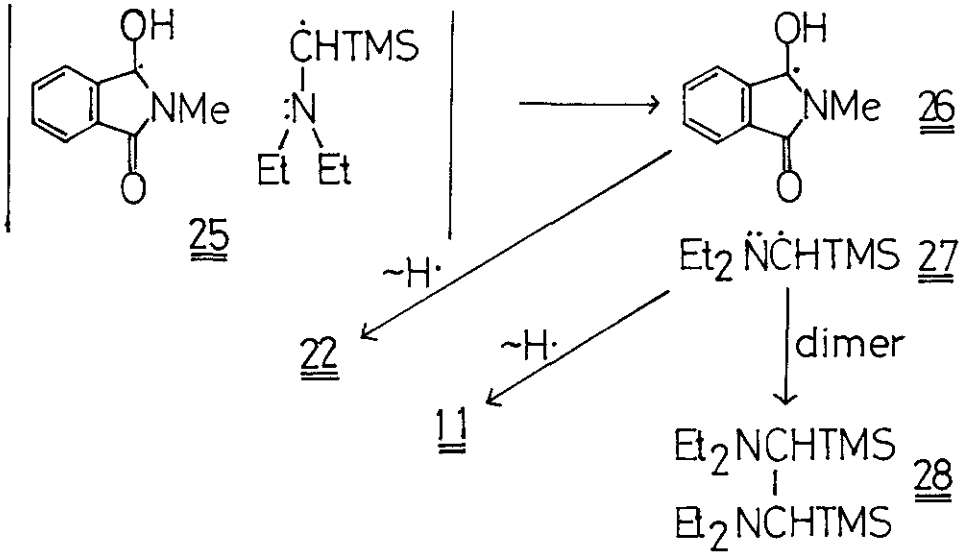
Irradiation of a CH_3CN solution of phthalimide (**4a**) and α-silyl thioether **10**, containing a trace amount of HCl was performed in order to gain information about the pathway used for formation of olefinic products. None of photoadduct **15** was detected in this reaction mixture and only the elimination products **17** and **19** were formed. Further, when the isolated pure photoadduct **15** was stirred in CH_3CN or CH_2Cl_2 solutions containing HCl at room temperature, elimination (dehydration) occurred to give a diastereomeric mixture of olefinic products **17** and **19** in a similar ratio to that observed in the photochemical reaction. However, the presence of solid $NaHCO_3$ in CH_3CN photolysis solution of phthalimide (**4a**) and α-silyl thioether **10** did not lead to a significant change in the photoadduct compositions ; photoproducts **15**, **17**, and **19** were generated. This observations suggest that olefinic products 17 and 19 are formed via elimination of H_2O or trimethylsilanol which is facilitated by the presence of acid. The lack of effect by $NaHCO_3$ seems to be somewhat difficult to understand. However, for photoreaction in CH_3OH solution of phthalimide (4b) and α-silyl ether 9, the presence of $NaHCO_3$ blocks formation of olefinic product 14 while the presence of acid causes olefin 14 to be the exclusive product. These results indicate that the sulfur atoms β to hydroxy carbons in 15 and 16 or β to silyloxy carbons in 24a, b renders the β-protons more highly acidic as compared to those in the oxygen analog 13 which results in elimination even under basic conditions.

Photoreaction of Phthalimide with α-Silylamine in Nonpolar Solvents.

Only non-silicon containing photoadducts are formed in the photoreaction of phthalimides (4a, b) with α-silylheteroatom compounds 9~11 in CH_3OH and CH_3CN. The results are similar to those observed in studies of the photoinduced SET reactions of iminium salt[1d] and arenecarbonitriles[2] with these silicon containing electron donors. In these processes the intermediate cation radicals undergo selective desilylation leading to non-silicon containing adducts. These results stand in contrast to those made in studies of the SET photochemistry of cyclohexenones with α-silylamine 11[3] which showed that two pathways involving α-deprotonation and α-desilylation of the intermediate amine cation radical compete and that deprotonation is predominant in aprotic, nonpolar solvents such as CH_3CN, CH_2Cl_2, and cyclohexane while α-desilylation is favorable in protic, polar solvent such as CH_3OH and H_2O-CH_3OH. In this regard it is especially significant that photoreaction of 4a with α-silylamine 11 in CH_3CN gives rise to the non-silicon containing adduct 21 exclusively. In order to probe this process further we have examined the photoaddition reaction of α-silylamine 11 and phthalimide (4a) in solvents such as n-hexane (E_T30.9) and CH_2Cl_2 (E_T41.1) which are more nonpolar than the aprotic solvent, CH_3CN (E_T46.0).[7] we felt tnat these conditions would facilitate CIP formation and reaction. In the silylamine-enone systems CIP - reaction is known to favor proton transfer from the cation to anion radical partners.[3]

Photoreduced product, 3-phthalimidine (22) was the only observable product to be formed from the reaction of 4a with 11 in n-hexane (83% yield). No silicon containing photoadduct was observed. It is possible that the photoreduced product 22 could be formed by proton transfer in the α-silylamine radical cation-phthalimide radical anion CIP in hexane. Thus, the phthalimide radical anion could undergo cage escape and H atom abstraction to give 3-phthalimidine (22) to the exclusion of in-cage coupling of radical pair 25 owing to the bulkiness of TMS-substituted α-amino radical 27 (Scheme 4).

Scheme 4.



During study on the SET photochemistry of cyclohexenone- α-silylamine (11) systems, the carvone anion radical was observed to suffer difficulty in coupling with TMS substituted α-amino radical 27. The TMS amine radical 27 was observed to dimerize to give bis-TMS amine dimer 28.[3b] We might expect that an out-caged TMS amine radical 27 formed in the phthalimide reaction would also dimerize to form 28. We checked for the formation of dimer 28 as possible evidence for α-deprotonation of amine radical cation generated in the reaction of phthalimide-α-silylamine. However we could not detect the dimer 28 in the photoreaction mixture. The photoreaction of phthalimide (4a) with α-silylamine 11 in hexane appears to follow a quite different reaction route to form the reduced phthalimide.

Thus it seems to be somewhat difficult to conclude that nonpolar solvent, n-hexane does not lead to favorable α-deprotonation of α-silylamine radical cation. However irradiation of CH_2Cl_2 solutions of the phthalimide and silylamine resulted in formation of 21 and 22, a result similar to that arising in the CH_3CN reaction. Thus, silyl group transfer is still the exclusive pathway in reaction conducted in the nonpolar media.

DISCUSSION

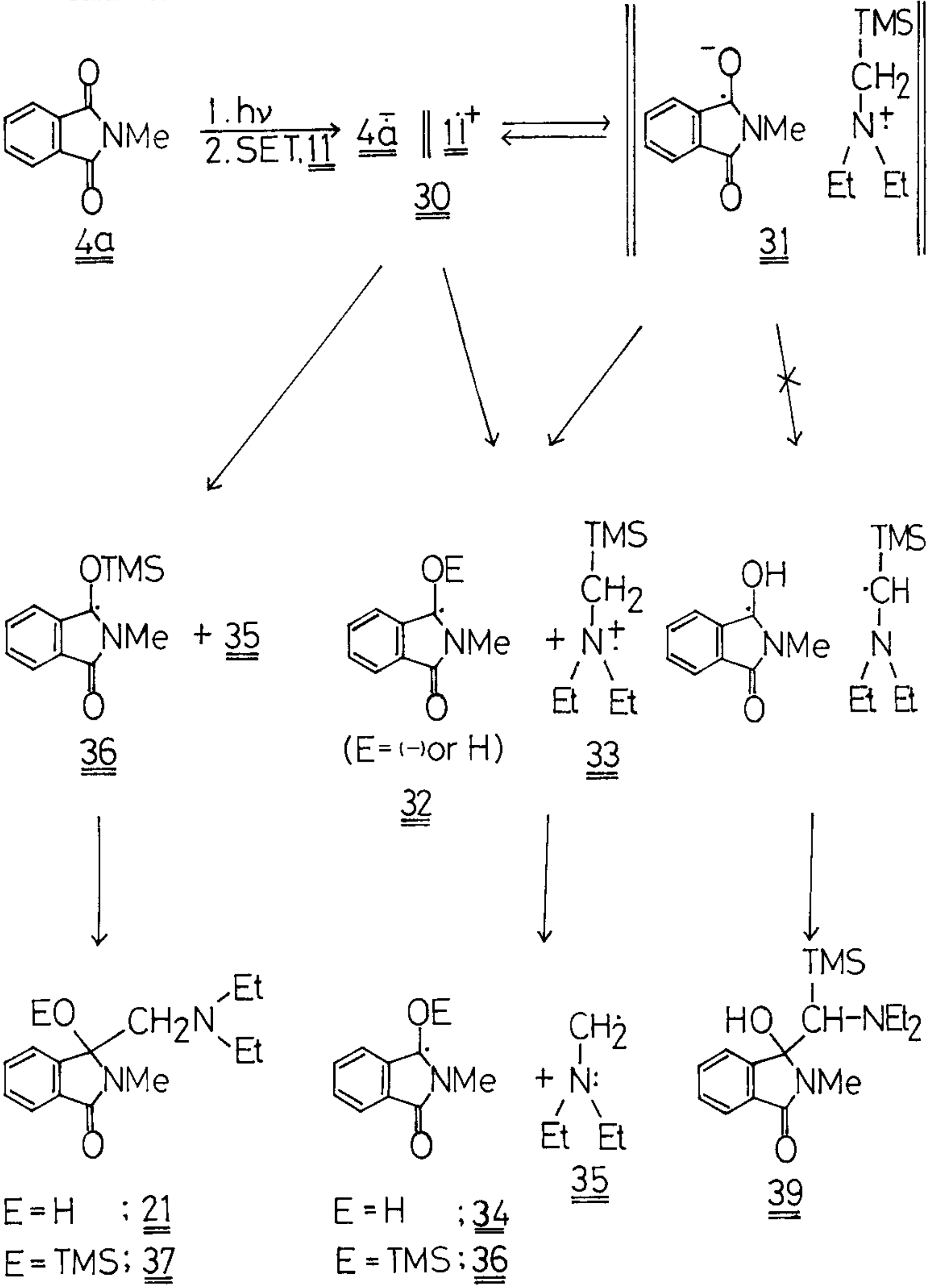
The observations presented above show that phthalimides participate in photoaddition with α-silyl ether, α-silyl thioether and α-silylamine substrates. Reactions of phthalimides with the α-silyl-n-electron donors are highly chemoselective, leading to adducts 7 (Scheme 3) in which phthalimidinyl units are bonded to the α-carbon in place of the trimethylsilyl group. In some cases the photoadducts undergo elimination to yield olefinic products in a secondary ground state reaction. In all cases, except for phthalimide (4b)-α-silylamine (11) photoreaction, photoadditions occur in moderate to high yields. The nature of photoadducts along with an analysis of excited state and ground state electrochemical potentials suggests that these reactions follow electron transfer mechanisms. Accurate quantum efficiencies of the SET-induced photoaddition of phthalimides with α-silyl-n-electron donors, were not determined and thus their relative efficiencies could not be compared with a high degree of accuracy. However the photoreactions of 4a and 4b with α-silyl amine 11 and α-silyl thioether 10 appear to be ca. 3-5 times more efficient than that with α-silyl ether 9 judging from irradiation times and phthalimide conversions (Table 1). Based upon donor oxidation potentials, the free energy for SET to excited phthalimide[9] should become less negative in the series α-silylamine 11 α-silyl thioether[10] 10 α-silyl ether[11] 9. The low reactivity of α-silyl ether 9, in this series appears to correlate with its highest oxidation potential. The free energy for SET from 9 to phthalimide (4b) is calculated[8] to be close to zero which explains why in CH_3CN solution phthalimide (4b) and α-silyl ether 9 are photochemically unreactive. However SET-induced photoreaction of this pair does occur in the more polar CH_3OH.
The observations made for the photoreaction of phthalimides with α-silyl thioether

10 in the presence of acid and in the acid treatment experiment of phthalimidine product, 15 strongly suggest that the precursors of olefinic products are initially formed photoadducts 15 and 16, respectively. The alternate route to these products involving a Peterson type elimination[12] of silicon containing photoadduct 8 (XR = S-n-Pr) seems less likely. Peterson type eliminations often require strong bases and higher temperatures than those present under the photoreaction conditions.

Importantly in the reactions of phthalimides with α-silyl-n-electron donors, silicon containing photoadducts 8[13] are not generated *via* sequential SET- α-deprotonation pathway. The observed exclusive chemoselectivity towards α-desilylation can be attributed to the lower basicity of phthalimide radical anions and to a preferential conformation of intermediate contact ion pairs which favor silyl rather than proton transfer. SET-photoreaction of phthalimides - α-silyl-n-electron donors can be thought to follow a mechanism (Scheme 5) analogous to that employed in the photochemistry of cyclohexenones- α-silylamine systems. Electron transfer between α-silyl donor (e.g. 11) and excited phthalimide (e.g. 4a) results in generation of the solvent separated ion pair (SSIP) 30 which can transform to contact ion pair (CIP) 31 or free ion radicals 32 and 33. In media of high polarity,[14,15] formation of free ions 32 and 33 from the SSIP 30 is likely. On the other hand in solvents of low polarity, generation of the CIP 31 should be favored. Preferential desilylation either with solvent as a nucleophile or liberating a short-lived silenium cation in SSIP 30 and/ or free radical ion 33 is expected based on the observations made by Yoshida.[16] Unlike the case of a CIP formed by SET in the cyclohexenone- α -silylamine systems, proton transfer between ion radicals in the CIP 31, should not be favorable due to low basicity of phthalimide radical anion[17] and perhaps unfavorable conformational interaction of α-proton with oxy anion in the CIP 31. The pk_b value of phthalimide radical anion is expected to be less than the reported value of 7.7[17] for the benzamide radical anion due to inductive effect by the second carbonyl group on the imide nitrogen. Thus, phthalimide radical anion having a lower pk_b than 7.7 should not be able to effectively deprotonate the amine radical cation which has a pk_a values in the range of 8[18].

Thus, the lower basicity of phthalimide radical anion and perhaps a conformational arrangement in the CIP favoring preferential Si-O bonding combine to result in

Scheme 5.


NMe
4a
1. hν
2. SET, 11
4a⁻ ‖ 11⁺
30
⁻O
NMe
TMS
CH2
N⁺
Et Et
31
OTMS
NMe
+ 35
36
OE
NMe
(E = (−) or H)
32
TMS
CH2
+ N⁺
Et Et
33
OH
NMe
TMS
·CH
N
Et Et
EO
CH2N
Et
Et
NMe
E = H ; 21
E = TMS ; 37
OE
NMe
E = H ; 34
E = TMS ; 36
CH2·
+ N:
Et Et
35
TMS
HO
CH-NEt2
NMe
39

silyl transfer in the CIP. Similar reasoning could also be employed to explain the selective desilylation seen in reactions with α-silyl ether **9** and α-silyl thioether **10**. We are continuing investigations in this area to determine the factors that control partitioning of silyl substituted cation radicals between α-deprotonation and α-desilylation pathways.

EXPERIMENTAL SECTION

General procedures

Nmr spectra were recorded by using Varian EM-360, Bruker WP-200 spectrometers, *and chemical shifts are reported in values in parts per million downfield from* tetramethylsilane employed as internal standard. Preparative photolysis was conducted with an apparatus consisting of a 450W Hanovia medium mercury vapor lamp surrounded by a Pyrex filter in a quartz immersion well under inert atmospheres and solvent used for photolysis was removed under reduced pressure. Low resolution mass spectral analyses were performed at 70eV on Hitachi RMU-6 mass spectrometer. High resolution mass spectral analyses were performed at 70eV on Hitachi VG-7070 mass spectrometer or the Penn State Univ. mass spectrometry center. Drying of organic layers obtained by work-up of reaction mixtures was performed by standing over anhydrous sodium sulfate. Preparative TLC was performed on 20 x 20cm plates coated with E-Merck silica gel PF_{254}. Trimethylsilylmethyl ethyl ether (**9**)[19], trimethylsilylmethyl n-propyl thioether (**10**)[20] and N-trimethylsilylmethyl-N, N-diethylamine (**11**)[3] were prepared by the reported methods.

Irradiation of N-methylphthalimide (**4a**) with trimethylsilylmethyl ethyl ether (**9**) in CH_3OH

N-Methylphthalimide (**4a**, 400 mg, 2.48 mmol) and $TMSCH_2OCH_2CH_3$ (**9**, 1600 mg, 12 mmol) were dissolved in 200 ml of CH_3OH and irradiated for 4h resulting 62% conversion. After removal of CH_3OH, the residue was subjected to preparative tlc (silica gel, 5% CH_3OH in CH_2Cl_2) to yield 200 mg (40%) of **12** as a white crystal, mp 81-83 °C. Spectral data for **12** ; ^{1}H-nmr ($CDCl_3$), 1.00 (t, J=7Hz, 3H, $-OCH_2C\underline{H}_3$), 2.69 (s, 3H, $N-CH_3$), 3.35(q, J=7Hz, 2H, $-OC\underline{H}_2CH_3$), 3.61 and 3.70 (two d, J=10Hz, two diastereotopic $-C-C\underline{H}_2-O$), 4.40 (br. s, 1H, OH), 7.30-7.70 (m, 4H, aromatic) ; ir (neat) 3600-3200 (br. OH stretching), 1670 cm^{-1} (C=O stretching) ; ^{13}C-nmr ($CDCl_3$), 14.8 (q, $OCH_2\underline{C}H_3$), 23.9 (q, $N-\underline{C}H_3$), 67.2 (t, $O-\underline{C}H_2CH_3$), 72.2 (t, $-\underline{C}H_2OCH_2CH_3$), 88.7 (s, C-3), 122.2 (d), 122.9 (d), 129.4 (d), 131.4 (s), 131.8 (d), 145.7(s), 167.6 (C=O) ; mass spec., m/z (rel. intensity) 221 (M^+, 0.46), 203 ($M^+ -H_2O$, 68), 174 ($M^+ -H_2O-.CH_2CH_3$, 100), 162 (12), 161 (13), 146 (33), 117 (17) ; high resolution mass spec., m/z 221.1030 ($C_{12}H_{15}NO_3$ requires 221.1052).

Irradiation of N-methylphthalimide (**4a**) with trimethylsilylmethyl ethyl ether (**9**) in CH_3CN

N-Methylphthalimide (**4a**, 400 mg, 2.48 mmol) and $TMSCH_2OCH_2CH_3$ (**9**, 1600 mg, 12 mmol) were dissolved in 200 ml of CH_3CN and irradiated for 13h resulting 48% conversion. After removal of CH_3CN, the residue was subjected to preparative tlc (silica gel, 5% CH_3OH in CH_2Cl_2) to yield 70 mg (27%) of **12**.

Irradiation of N-methylphthalimide (**4a**) with trimethylsilylmethyl n-propyl thioether (**10**) in CH_3OH

N-Methylphthalimide (**4a**, 300 mg, 1.86 mmol) and $TMSCH_2SCH_2CH_2CH_3$ (**10**, 1500 mg, 9.26 mmol) were dissolved in 200 ml of CH_3OH and irradiated for 1h resulting 75% conversion. After removal of CH_3OH, the residue was subjected to preparative tlc (silica gel, 4% CH_3OH in CH_2Cl_2) to yield 257 mg (78%) of **15** as a pale yellow crystal, mp 67-69 °C. Spectral data for 15 ; ^{1}H-nmr (CCl_4), 0.74 (t, J=7.2Hz, 3H, $-CH_2CH_2C\underline{H}_3$), 1.32 (sext, J=7.2Hz, 2H, $-CH_2C\underline{H}_2CH_3$), 2.04 (t, J=7.2) Hz, 2H, $-C\underline{H}_2CH_2CH_3$), 2.62 (s, 3H, N-$CH_3$), 2.95 and 3.14 (two d, J=14Hz two diastereotopic -C-CH_2-S), 5.30 (br. s, 1H, OH), 7.20-7.70 (m, 4H, aromatic) ; ir (neat) 3600-3150 (OH stretching), 1680 cm^{-1} (C=0 stretching) ; ^{13}C-nmr ($CDCl_3$), 13.0 (q, $-SCH_2CH_2\underline{C}H_3$), 22.7 (t, $S-CH_2\underline{C}H_2CH_3$), 23.3 (q, N-$\underline{C}H_3$), 35.1 (t, $-S-\underline{C}H_2-CH_2CH_3$), 38.1 (t, $-\underline{C}H_2-S-$), 90.1 (s, HO-$\underline{C}$), 121.9 (d), 122.8 (d), 129.4 (d), 131.5 (s), 131.8 (d), 146.1 (s), 167.4 (s, C=O) ; mass spec., m/z (rel. intensity) 234 (M^+-H_2O, 85), 233 (100), 190 (29), 162 (25), 159 (15), 146 (13) ; high resolution mass spec., m/z 251.0975 ($C_{13}H_{17}O_2NS$ requires 251.0981).

Irradiation of N-methylphthalimide (4a) with trimethylsilylmethyl n-propyl thioether (10) in CH_3CN

N-Methylphthalimide (4a, 300 mg, 1.86 mmol) and $TMSCH_2SCH_2CH_2CH_3$ (10, 1500 mg, 9.26 mmol) were dissolved in 200 ml of CH_3CN and irradiated for 2h resulting 48% conversion. After removal of CH_3CN, the residue was subjected to preparative tlc (silica gel, 3% CH_3OH in CH_2Cl_2) to yield 101 mg (46%) of 19 as a white crystal, mp 116-118 °C, 57 mg (26%) of 17 as a pale yellow crystal, mp 62-63 °C, and 37 mg (17%) of 15 as a crystal. Spectral data for 19 ; ^{1}H-nmr (CCl_4), 1.10 (t, J=7Hz, 3H, $-SCH_2CH_2C\underline{H}_3$), 1.80 (sext, J=7Hz, 2H, $-S-CH_2C\underline{H}_2CH_3$), 2.80 (t, J=7Hz, 2H, $-S-C\underline{H}_2CH_2CH_3$), 3.55 (s, 3H, N-$CH_3$), 5.90 (s, 1H, alkenic), 7.20-7.80 (m, 4H, aromatic) ; ir (KBr) 3020 (alkenic C-H stretching), 1660 cm^{-1} (C=0 stretching) ; ^{13}C-nmr ($CDCl_3$), 13.0(q, $-SCH_2CH_2\underline{C}H_3$), 23.4 (t, $-SCH_2\underline{C}H_2CH_3$), 28.9 (q, N-$\underline{C}H_3$), 38.2 (t, $-S-\underline{C}H_2CH_2CH_3$), 105.2 (d, $=\underline{C}$-H), 118.2 (d), 123.0 (d), 127.3 (s), 127.8(d), 131.3 (d), 133.2 (s), 136.1 (s), 167.5 (s, C=0) ; mass spec., m/z (rel. intensity) 233 (M^+,100), 190 ($M^+-\cdot CH_2CH_2CH_3$, 77), 174 (11), 162 (19), 159 (23), 158 (42) ; high resolution mass spec., m/z 233.0880 ($C_{13}H_{15}NOS$ requires 233.0875). Spectral data for 17; ^{1}H-nmr (CCl_4), 1.05 (t, J=7Hz, 3H, $-SCH_2CH_2C\underline{H}_3$), 1.75 (sext, J=7Hz, 2H, $-SCH_2C\underline{H}_2CH_3$), 2.75 (t, J=7Hz, 2H, $-SC\underline{H}_2CH_2CH_3$), 3.18 (s, 3H, N-$CH_3$), 5.70 (s, 1H, alkenic), 7.20-8.20 (m, 4H, aromatic) ; ir (KBr) 3050 (alkenic C-H stretching), 1680 cm^{-1} (C=O stretching) ; ^{13}C-nmr ($CDCl_3$), 13.1 (q, $-SCH_2CH_2\underline{C}H_3$), 23.4 (t, $-S-CH_2\underline{C}H\ CH_3$), 25.9 (q, $N-\underline{C}H_3$), 37.9 (t, $S-\underline{C}H_2CH_2CH_3$), 107.4 (d, $C=\underline{C}H$), 123.1 (d), 124.1 (d), 128.4 (d), 129.9 (s), 131.7(d), 134.1 (s), 134.7 (s), 165.9 (s, C=O) ; mass spec., m/z (rel. intensity) 233 (M^+, 100), 190 ($M^+ - \cdot CH_2CH_2CH_3$, 78), 174 (25), 162 (23), 161 (38), 159 (24), 158 (41), 149 (29), 146 (39) ; high resolution mass spec., m/z 233.0875 ($C_{13}H_{15}NOS$ requires 233.0875). Photoproducts 19 and 17 isomerized to another geometric isomers 17 and 19 respectively on standing in nmr tube at room temperature.

Irradiation of N-methylphthalimide (4a) with trimethylsilylmethyl n-propyl thioether (10) in CH_3CN containing $NaHCO_3$.

N-Methylphthalimide (4a, 20 mg, 0.124 mmol) and $TMSCH_2SCH_2CH_2CH_3$ (10, 100 mg, 0.617 mmol) were dissolved in 20 ml of CH_3CN containing a trace of $NaHCO_3$ and irradiated for 1.5h. After removal of CH_3CN, the residue was checked by tlc to observe photoproducts 15, 17 and 19 in a similar ratio to that in irradiation without $NaHCO_3$.

Irradiation of N-methylphthalimide (4a) with trimethylsilylmethyl n-propyl thioether (10) in CH_3CN containing HCl.

N-Methylphthalimide (4a, 20 mg, 0.124 mmol) and $TMSCH_2SCH_2CH_2CH_3$ (10, 100 mg, 0.617 mmol) were dissolved in 20 ml of CH_3CN containing a trace of HCl and irradiated for 1.5h. After removal of CH_3CN, the residue was dissolved in 5 ml of 5% aqueous NaOH solution and extracted with 20 ml of CH_2Cl_2. After removal of CH_2Cl_2 under reduced pressure, the residue was checked by tlc to observe exclusive formation of 17 and 19.

Dehydration of photoadduct, **15** in the presence of HCl

The photoadduct **15** was dissolved in 10 ml of CH_3CN or CH_2Cl_2 containing a trace of HCl and stirred in room temperature for 10 min. After removal of CH_3CN or CH_2Cl_2, the residue was dissolved in 5 ml of 5% aqueous NaOH solution and extracted with 20 ml of CH_2Cl_2. After removal of CH_2Cl_2 under reduced pressure, the residue was checked by tlc to observe the formation of **17** and **19** in ca. 2:1 ratio.

Irradiation of N-methylphthalimide (**4a**) with trimethylsilylmethyldiethylamine ($TMSCH_2N(CH_2CH_3)_2$, **11**) in CH_3CN

N-Methylphthalimide (**4a**, 300 mg, 1.86 mmol) and $TMSCH_2N(CH_2CH_3)_2$ (**11**, 883 mg, 5.55 mmol) were dissolved in 200 ml of CH_3CN and irradiated for 2h resulting 97% conversion. After removal of CH_3CN, the residue was subjected to preparative tlc (silica gel, 4% CH_3OH in CH_2Cl_2) to yield 183 mg (41%) of **21** as a white crystal, mp 106-107 °C, and 66 mg (22%) of **22** as a white crystal, mp 129-130 °C (lit.[6a] mp 130-131 °C). Spectral data for **21** ; ^1H-nmr ($CDCl_3$), 0.80 (t, J=7Hz, 6H, $N(CH_2C\underline{H}\ )_2$), 2.40 (q, J=7Hz, 4H, $N(C\underline{H}_2CH_3)_2$), 2.73 (s, 3H, $N\text{-}C\underline{H}_3$), 2.75 and 2.85 (two s, diastereotopic $-CH_2-N$), 4.67 (br. s, 1H, OH), 7.20-7.70 (m, 4H, aromatic) ; ir (neat) 3650-3150 (OH stretching), 1675 cm^{-1} (C=O stretching) ; ^{13}C-nmr ($CDCl_3$), 11.7 (q, $N\text{-}CH_2\underline{C}H_3$), 23.9 (q, $N\text{-}\underline{C}H_3$), 48.1 (t, $N\text{-}\underline{C}H_2CH_3$), 59.4 (t, $\underline{C}H_2\text{-}N$), 88.8 (s, $\underline{C}$-OH), 122.3 (d), 122.8 (d), 129.0 (d), 131.5 (d), 131.7 (s), 147.9 (s), 167.3 (s, C=0) ; mass spec., m/z (rel. intensity) 248 (M^+, 0.21), 230 (M^+-H_2O, 74), 215 ($M^+-H_2O-CH_3$, 24), 201 ($M^+-H_2O-CH_3CH_2$, 48), 161 (24), 146 (21), 130 (6), 117 (8), 86 ($CH_2=\overset{+}{N}Et_2$, 100) ; high resolution mass spec., m/z 248.1511 ($C_{14}H_{20}N_2O_2$ requires 248.1525). Spectral data for **22** ; ^1H-nmr ($CDCl_3$), 2.89 (s, 3H, $N\text{-}C\underline{H}_3$), 4.78 (br. s, 1H, OH), 5.58 (s, 1H, methine), 7.33-7.63 (m, 4H, aromatic) ; ir (KBr) 3600-3100 (OH stretching), 1645 cm^{-1} (C=0 stretching) ; ^{13}C-nmr ($CDCl_3$), 26.0 (q, $N\text{-}\underline{C}H_3$), 83.6 (d, $\underline{C}H$-OH), 123.0 (d), 123.2 (d), 129.6 (d), 131.3 (s), 132.1 (d), 143.8 (s), 167.6 (s, C=0).

Irradiation of N-methylphthalimide (**4a**) with trimethylsilylmethyldiethylamine ($TMSCH_2N(CH_2CH_3)_2$, **11**) in CH_3OH

N-Methylphthalimide (**4a**, 300 mg, 1.86 mmol) and $TMSCH_2N(CH_2CH_3)_2$ (**11**, 883 mg, 5.55 mmol) were dissolved in 200 ml of CH_3OH and irradiated for 2h resulting 86% conversion. After removal of CH_3OH, the residue was subjected to preparative tlc (silica gel, 3% CH_3OH in CH_2Cl_2) to yield 84 mg (33%) of **22**.

Irradiation of N-methylphthalimide (**4a**) with trimethylsilylmethyldiethylamine ($TMSCH_2N(CH_2CH_3)_2$, **11**) in CH_2Cl_2

N-Methylphthalimide (**4a**, 300 mg, 1.86 mmol) and $TMSCH_2N(CH_2CH_3)_2$ (**11**, 883.5 mg, 5.55 mmol) were dissolved in 200 ml of CH_2Cl_2 and irradiated 2h resulting 52% conversion. After removal of CH_2Cl_2, the residue was subjected to preparative tlc (silica gel, 3% acetone in CH_2Cl_2) to yield 49 mg (20%) of **21** and 48 mg (30%) of **22**.

Irradiation of N-methylphthalimide (**4a**) with trimethylsilylmethyldiethylamine ($TMSCH_2N(CH_2CH_3)_2$, **11**) in n-hexane

N-Methylphthalimide (**4a**, 200 mg, 1.24 mmol) and $TMSCH_2N(CH_2CH_3)_2$ (**11**, 589 mg, 3.70 mmol) were dissolved in 180 ml of hexane and irradiated for 1.5h resulting 54.5% conversion. After removal of hexane, the residue was subjected to preparative tlc (silica gel, 3% CH_3OH in CH_2Cl_2) to yield 91 mg (82.5%) of **22**.

Irradiation of phthalimide (**4b**) with trimethylsilylmethyl ethyl ether (**9**) in CH_3OH

Phthalimide (**4b**, 400 mg, 2.72 mmol) and $TMSCH_2OCH_2CH_3$ (**9**, 1080 mg, 8.18 mmol) were dissolved in 200 ml of CH_3OH and irradiated for 2h resulting 47% conversion. After removal of CH_3OH, the residue was subjected to preparative tlc (silica gel, 3% CH_3OH in CH_2Cl_2) to yield 30 mg (12%) of **13** as a viscous oil and 82 mg (36%) of **14** as a white crystal, mp 128~130 °C. Spectral data for **13** : ^{1}H-nmr ($CDCl_3$), 1.15 (t, J=7Hz, 3H, $-OCH_2C\underline{H}_3$), 3.50 (q, J=7Hz, 2H, $-OC\underline{H}_3CH_3$), 3.65 and 3.70 (two s, 2H, diastereotopic $C-C\underline{H}_2-O-$), 5.40 (br. s, 1H, OH), 7.30-7.70 (m, 5H, aromatic and NH) ; ir (KBr) 3650-3150 (br. OH and NH stretching), 1705 cm^{-1} (C=O stretching). Spectral data for **14** ; ^{1}H-nmr ($CDCl_3$), 1.36 (t, J=7Hz, 3H, $-OCH_2C\underline{H}_3$), 4.05 (q, J=7Hz, 2H, $-OC\underline{H}_2CH_3$), 6.54 (s, 1H, alkenic), 7.30-7.90 (m, 4H, aromatic), 8.20 (br. s, 1H, NH) ; ir (KBr) 3600-3100 (NH stretching), 1705 cm^{-1} (C=O stretching) ; ^{13}C-nmr ($CDCl_3$), 15.3 (q, $-OCH_2\underline{C}H_3$), 69.7 (t, $-O\underline{C}H_2-CH_3$), 117.5 (s), 118.1 (d), 123.8 (d), 127.1 (d), 128.5 (s), 128.8 (d), 131.5 (d) 136.5 (s), 166.9 (s, C=O) ; mass spec., m/z (rel. intensity) 189 (M^+, 90), 161 (16), 160 ($M^+-CH_3CH_2$, 100), 148 (14), 147 (23), 133 (21), 132 (86), 130 (19), 105 (18), 104 (57), 103 (45), 102 (11) ; high resolution mass spec., m/z 189.0790 ($C_{11}H_{11}O_2N$ requires 189.0790).

Irradiation of phthalimide (**4b**) with trimethylsilylmethyl ethyl ether (*$TMSCH_2OCH_2CH_3$* **9**) *in CH_3OH containing* $NaHCO_3$

Phthalimide (**4b**, 20 mg, 0.136 mmol) and $TMSCH_2OCH_2CH_3$ (**9**, 54 mg, 0.41 mmol) were dissolved in CH_3OH (15 ml) with a trace of $NaHCO_3$ and irradiated for 2h. After removal of CH_3OH, solid residue was checked by tlc to observe photoproduct **13**.

Irradiation of phthalimide (4b) with trimethylsilylmethyl n-propyl thioether (10) in CH_3OH

Phthalimide (4b, 400 mg, 2.72 mmol) and $TMSCH_2SCH_2CH_2CH_3$ (10, 880 mg, 5.43 mmol) were dissolved in 250 ml of CH_3OH and irradiated for 40 min resulting 79% conversion. After removal of CH_3OH, the residue was subjected to preparative tlc (silica gel, 5.5% CH_3OH in CH_2Cl_2) to yield 453 mg (85%) of 16 as a white crystal, mp 91-92 °C. Spectral data for 16 ; ^1H-nmr ($CDCl_3$), 0.87 (t, J=7.3Hz, 3H, $-SCH_2CH_2C\underline{H}_3$), 1.49 (sext, J=7.3Hz, 2H, $-SCH_2C\underline{H}_2CH_3$), 2.47 (t, J=7.3Hz, 2H, $SC\underline{H}_2CH_2CH_3$), 2.88 and 3.20 (two d, J=14Hz, 2H, diastereotopic $C-C\underline{H}_2S-$), 5.28 (br. s, OH), 7.30-7.60 (m, 4H, aromatic), 7.72 (s, NH) ; ir (neat) 3600-3100 (NH and OH stretching), 1710 cm^{-1} (C=O stretching) ; ^{13}C-nmr ($CDCl_3$), 13.2 (q, $-SCH_2CH_2\underline{C}H_3$), 22.9 (t, $-SCH_2\underline{C}H_2CH_3$), 36.2 (t, $-S\underline{C}H_2CH_2CH_3$), 41.0 (t, $C-\underline{C}H_2S$), 88.1 (s, $HO-\underline{C}-CH_2$), 122.1 (d), 123.4 (d), 129.6 (d), 130.6 (s), 132.6 (d), 147.7 (s), 169.5 (s, C=O) ; mass spec., m/z (rel. intensity) 219 (M^+-H_2O, 31), 177 (21), 149 (15), 148 (100), 145 (13), 130 (94), 103 (10), 102 (31), 90 (97), 61 (24) ; high resolution mass spec., m/z 219.0718 ($C_{12}H_{15}NS-H_2O$ requires 219.0719).

Irradiation of phthalimide (4b) with trimethylsilylmethyl n-propyl thioether (10) in CH_3CN

Phthalimide (4b, 400 mg, 2.72 mmol) and $TMSCH_2SCH_2CH_2CH_3$ (10, 880 mg, 5.43 mmol) were dissolved in 250 ml of CH_3CN and irradiated for 2h resulting 12.5% conversion. After removal of CH_3CN, the residue was subjected to preparative tlc (silica gel, 2.5% CH_3OH in CH_2Cl_2) to yield 38 mg (47%) of 16 as a crystal, 25 mg (34%) of 20 as a pale yellow crystal, mp 109-111 °C, and 12 mg (16%) of 18 as a pale yellow crystal, mp 121-122 °C. Spectral data for 20; ^1H-nmr ($CDCl_3$), 1.03 (t, J=7.2Hz, 3H, $-SCH_2CH_2C\underline{H}_3$), 1.72 (sext, J=7.2Hz, 2H, $-SCH_2C\underline{H}_2CH_3$), 2.79 (t, J=7.2Hz, 2H, $-SC\underline{H}_2CH_2CH_3$), 6.19 (s, 1H, alkenic), 7.35-8.25 (m, 4H, aromatic), 9.30 (s, 1H, NH) ; ir (KBr) 3200 (NH stretching), 1670 cm^{-1} (C=O stretching) ; mass spec., m/z (rel. intensity) 219 (M^+, 100), 177 (85), 176 ($M^+-CH_3CH_2CH_2^{\cdot}$, 31), 149 (20), 148 (44), 145 (26), 132 (39), 130 (13), 121 (12), 104 (18), 103 (17), 89 (11) ; high resolution mass spec., m/z 219.0710 ($C_{12}H_{13}ONS$ requires 219.0712). Spectral data for 18; ^1H-nmr ($CDCl_3$), 1.00 (t, J=7.3Hz, 3H, $S-CH_2CH_2C\underline{H}_3$), 1.69 (sext, J=7.3Hz, 2H, $S-CH_2C\underline{H}_2CH_3$), 2.78 (t, J=7.3Hz, 2H, $S-C\underline{H}_2CH_2CH_3$), 6.10 (s, 1H, alkenic), 7.32-7.85 (m, 4H, aromatic), 8.30 (br. s, 1H, NH) ; ir (KBr) 3200 (NH stretching), 1680 cm^{-1} (C=O stretching); ^{13}C-nmr ($CDCl_3$), 13.1 (q, $-SCH_2CH_2\underline{C}H_3$) 23.5 (t, $-SCH_2\underline{C}H_2CH_3$), 37.0 (t, $-S\underline{C}H_2CH_2CH_3$), 102.4 (d), 119.3 (d), 123.6 (d), 129.2 (d), 129.6 (s), 132.0 (d), 134.2 (s), 136.1 (s), 167.8 (s, C=O); mass spec., m/z (rel. intensity) 219 (M^+, 47), 178 ($M^+-{\cdot}CH_2CH_2CH_3$, 7), 177 (46), 176 (19), 162 (100), 148 (42), 130 (60), 104 (32), 89 (30), 76 (46) ; high resolution mass spec., m/z 219.0718 ($C_{12}H_{13}ONS$ requires 219.0719).

Irradiation of phthalimide (4b) with trimethylsilylmethyldiethylamine (11) in CH_3OH or CH_3CN

Phthalimide (4b, 200 mg, 1.36 mmol) and $TMSCH_2N(CH_2CH_3)_2$ (11, 650 mg, 4.09 mmol) were dissolved in 180 ml of CH_3OH or CH_3CN and irradiated for 2h resulting 95% conversion. After removal of CH_3OH or CH_3CN, the residue was subjected to preparative tlc (silica gel, 10% CH_3OH in CH_2Cl_2) to yield 144 mg (75%) of 23 as a white crystal, mp 223-224 °C. Spectral data for 23 ; ^1H-nmr (DMSO-d_6), 3.15 (br. s, 2H, OH), 6.80-7.60 (m, 8H, aromatic), 8.35 (s, 2H, NH) ; ir (KBr) 3450-3100 (br. OH stretching), 3350 (NH stretching), 1680 cm^{-1} (C=O stretching) ; ^{13}C-nmr (DMSO-d_6) 89.8 (s, -C-OH), 122.2 (d), 123.6 (d), 129.3 (d), 131.3 (d), 132.8 (s), 146.0 (s), 167.9 (s, C=O) ; mass spec., m/z (rel. intensity) 278 (M^+-H_2O, 4), 263 (13), 147 (31), 104 (14), 105 (31), 84 (86), 76 (29), 66 (100).

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