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PHOTOCYCLIZATION OF METHYL 2-ARYLTHIO- AND 2-ARYLOXY-ACETOACETATES

A FACILE SYNTHESIS OF BENZOHETEROCYCLES[1]

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Abstract—A series of methyl 2-arylthio- (**2**) and 2-aryloxy-acetoacetates (**3**) have been prepared and their tautomeric equilibria have been examined by ^{1}H NMR spectroscopy. S-substitution at the α-position results in an increase of enol tautomer over 90%, while the O-analogoues exist predominantly in the keto form (Table 1). Pyrex-filtered irradiation of 2-arylthio compounds **2a-l** in benzene–methanol (1:1) solution gives benzothiophene derivatives (**6a-f, 7-10**) in fair yield except for **2j** and **2k**, for which photocyclization does not occur and only polymer formation is observed. A similar irradiation of O-analogues **3b** and **3c** affords the furan derivatives **17** and **18**, respectively, in rather low yield, whereas **3a** in photoinert under these conditions. Regiospecificity of photocyclization is revealed by the reactions of 2-naphthyl derivatives (**2h** and **3c**) which afford only naphto[2,1-b] isomer. A plausible reaction mechanism is also discussed.

S-Aryl vinyl sulfides are known to undergo photocyclization to give 5-membered S heterocycles.[2–5] Recently, Wolff revealed by flash photolytic studies that the reaction proceeds via the triplet excited state of the sulfides to colored dihydrothiophene intermediates which afford the final products by H-shifts or abstractions.[6] Intermediacy of thiocarbonyl ylides was also inferred by Schultz and DeTar[4] from results of chemical trapping experiments with dienophiles. The synthetic utility of these reactions called "heteroatom directed photoarylation" has been well presented by Schultz *et al.*[7,8]

α-Sulfenylated β-diketones and β-keto esters potentially have the structure of vinyl sulfides because of the enolizable property of the CO group.[9] We report details of our work on photochemistry of methyl 2-arylthio- and 2-aryloxy-acetoacetates, which provides a facile synthesis of benzothiophene derivatives.[10]

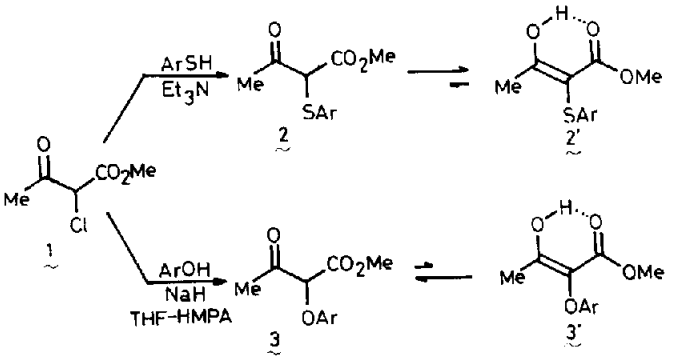
RESULTS AND DISCUSSION

Preparation and spectral properties of 2-substituted methyl acetoacetates

Most methyl 2-arylthioacetoacetates (**2a–k**) were prepared in high yield by the reaction of commercially available methyl 2-chloroacetoacetate (**1**) with appropriate arylmercaptanes in the presence of equimolar triethylamine. Compound **21** was obtained by the reaction of **1** and 8-quinolinethiol tin complex prepared from 8-quinolinesulfonyl chloride and stannous chloride.[11]

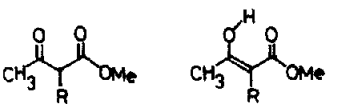
Because of decreased nucleophilicity of phenol relative to thiophenol, more vigorous conditions were required to effect the substitution for chlorine. Reaction of **1** with sodium phenoxides, prepared *in situ* from phenols and sodium hydride, in refluxing tetrahydrofuran (THF) solution containing one equiv of hexamethylphosphoramide (HMPA) gave methyl 2-aryloxyacetoacetates (**3a–c**) in moderate yields. The ^{1}H NMR spectral data of the α-substituted acetoacetates (**2** and **3**) are listed in Table 1 along with the data of some other related compounds.

The keto-enol tautomerism of β-keto esters has been studied by means of NMR spectroscopy.[9,12,13] It is known that α-substituents affect the tautomeric equilibrium of β-diketones by both steric and inductive effects.[9] Substitution of bulky or electron-donating groups at α-position reduces the enolization, whereas substitution of electron-withdrawing groups results in the increase of enol tautomer. The ^{1}H NMR data in Table 1 show the remarkable enol-increasing effect of sulfur. Introduction of an arylthio group at α-position of methyl acetoacetate results in a shift to over 90% enol tautomer,



Scheme 1.

Table 1. Enol percentage and ^{1}H NMR chemical shifts (δ values) of 2-substituted methyl acetoacetates in $CDCl_3$



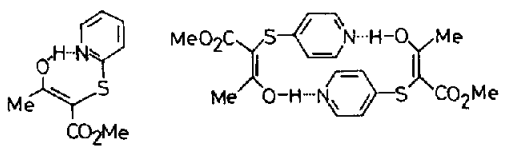
			keto[a]			enol[a]			
compd	R	enol%	CH_3	OCH_3	CH	CH_3	OCH_3	OH	others
1	-Cl	13	2.40	3.85	4.81	2.18	3.85	12.15	
2a	$-SC_6H_5$	95	2.33	3.74	4.52	2.33	3.74	13.72	6.98-7.42 (m,5H)
2b	$-SC_6H_4$-*p*-CH_3	100				2.33	3.74	13.71	2.29 (s,3H) 7.03 (s,4H)
2c	$-SC_6H_4$-*p*-OCH_3	86	2.35	3.87	4.38	2.35	3.74	13.60	3.74 (s,3H) 6.68-7.50 (m,4H)
2d	$-SC_6H_4$-*p*-F	93	2.35	3.79	4.43	2.35	3.76	13.66	6.75-7.15 (m,4H)
2e	$-SC_6H_4$-*p*-Cl	95	2.32	3.73	4.49	2.32	3.73	13.70	6.90-7.35 (m,4H)
2f	$-SC_6H_4$-*p*-Br	100				2.32	3.75	13.75	6.95,7.38 (A_2B_2,4H)[b]
2g	-S(1-naphthyl)	94	2.33	3.75	4.50	2.33	3.71	13.82	7.03 (dd,1H)[c] 7.18-7.95 (m,5H) 8.15-8.40 (m,1H)
2h	-S(2-naphthyl)	95	2.35	3.77	4.62	2.35	3.73	13.78	7.20-7.98 (m,7H)
2i	-S(2-pyridyl)	100[d]				2.31 2.40[e]	3.72 3.78[e]	13.76 5.5-5.9[e] (br)	6.81-7.65 (m,3H) 8.38 (dm,1H)[f]
2j	-S(4-pyridyl)	100[g]				2.31[e]	3.76[e]	11.5-12.5[e] (very br)	7.00 (dd,1H)[h] 8.41 (dd,1H)[h]
2k	-S(2-quinolyl)	82[i]	2.38	3.83	4.77	2.33 2.51[e]	3.72 3.85[e]	13.85 5.93[e] (br)	7.02-8.05 (m,6H)
2l	-S(8-quinolyl)	92	2.42	3.78	5.27	2.36	3.72	13.97	7.05-7.68 (m,4H) 8.16 (dd,1H),[j] 8.96 (dd,1H)[k]
3a	$-OC_6H_5$	20	2.29	3.75	4.92	1.95	3.68	11.18	6.71-7.42 (m,5H)
3b	-O(1-naphthyl)	27	2.45	3.81	5.62	1.99	3.66	11.40	6.67 (m,1H) 7.15-7.90 (m,5H) 8.34 (m,1H)
3c	-O(2-naphthyl)	26	2.42	3.84	5.24	2.02	3.72	11.36	7.02-7.89 (m,7H)
4[l]	$-NHC_6H_5$	38	2.28	--[n]	5.08	2.03	--[n]	12.36	6.47-6.90 (m,3H) 7.04-7.34 (m,2H)
5[m]	-H	0	2.08	---	4.67				

[a] All signals are sharp singlets unless otherwise noted. [b] J_{AB} = 8.8 Hz. [c] J = 7.5 and 2.0 Hz. [d] The ratio of cis/trans enols is 2.3. [e] Signals assigned to the trans enol. [f] J = 4.5 Hz. [g] This is composed of only trans enol. [h] J = 4.8 and 1.5 Hz. [i] The ratio of cis/trans enols is 2.0. [j] J = 8.3 and 1.5 Hz. [k] J = 4.5 and 1.5 Hz. [l] Reference [m] Reference 9. [n] The reported data are for the ethyl ester, keto; δ 1.23 (t) and 4.25 (q), enol; δ 1.13 (t) and 4.20 (q).

while the equilibrium is on the side of the keto tautomer for oxygen- (**3**) and nitrogen analogs (**4**). Methyl acetoacetate (**5**) (100% keto form) and most 2-alkyl derivatives also exist predominantly in the keto form.[9] Therefore, this unique effect of sulfur can be attributed to the stabilization of enol tautomer by sulfur conjugation,[14,15] while neither steric effect nor inductive effect gives reasonable explanation for these results.

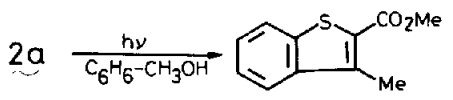
The enol OH proton shows a sharp singlet at very low magnetic field indicating the internally H-bonded conformers **2'** and **3'** (Scheme 1). Forsen and Nilsson[16] have shown that a linear relationship exists between the chelated CO stretching frequency and the chemical shift of the enol proton. A lower chemical shift of the enol OH corresponds to a stronger intramolecular H-bond.[9] In the case of **2i**, two kinds of enol signals were observed in the ratio of 2.3:1, but none of the keto tautomer. The broad OH signal (δ 5.5–5.9) of the minor enol (Table 1) suggests the *trans* conformation with a weaker intramolecular H bond with pyridine nitrogen as depicted in **2i'**. The *trans* enol of methyl acetoacetate was recently reported by Matusch.[12] The similar enol signals

were observed for the structurally related **2k** but **21**, in which such an intramolecular H-bond is not feasible, showed only signals due to the *cis* enol. The ^{1}H NMR spectrum of compound **2j** indicated the presence of only one enol conformer (Table 1). Although the spectrum was not changed over the measurable concentration range, the very broad signal of enol proton at δ 11.5–12.5 was considered to be a result of the intermolecular H-bond[17] via nitrogen, probably a bimolecular H-bond like **2j''**. This was also suggested by the photochemical inactivity of **2j** (*vide infra*).



2i'' 2j''

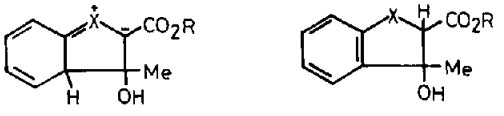
Photochemistry of methyl 2-arylthio- and 2-aryloxyacetoacetates. Irradiation of **2a** in benzene–methanol (1:1) solution under argon using a 100-W high pressure mercury lamp with a Pyrex filter gave benzothiophene **6a** (X = H, m.p. 104–105°)[18] in 66% yield as the sole product.



Scheme 2

The same photoreaction took place in a variety of solvents but in rather low yields: benzene (29%), acetone (21%), acetonitrile (19%), chloroform (21%) and methanol (41%).

Since aryl vinyl sulfides are well known to photocyclize via ylide intermediates,[4,6–8] the photoreaction of **2a** can be considered to occur from the enolic form present in tautomeric equilibrium with the keto form (Table 1) to give the thiocarbonyl ylide **11** (X = S, R = Me_3). The product is then formed either by direct dehydration of **11** or by the route via dihydrothiophene **12** (X = S, R = Me_3)[4,7] which would be easily dehydrated.

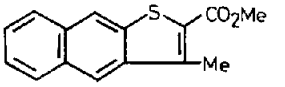


11 12

The similar photocyclization of the aza-analogues was reported by Schultz and Hagmann.[19,20] They isolated 3-hydroxyindoline **12** (X = Me_3, R = Et) by the photolysis of 2-anilinoacetoacetate in the absence of acids.[19] The β-hydroxy ketone intermediate was also spectroscopically observed for the selenium analog.[21] Irradiation of **2a** in n-hexane in the presence of sodium carbonate afforded only **6a** (29%) and no evidence for the presence of **12** (X = S, R = Me) was obtained by ^{1}H NMR analysis of the crude mixture. Furthermore, the attempt of trapping the ylide intermediates was unsuccessful. When a degassed benzene solution of **2a** (or **2h**) was irradiated in the presence of excess N-phenylmaleimide which is known to be a good dipolarophile,[4,22,23] N-phenylmaleimide was completely recovered and only benzothiophene **6a** (or **8**) was obtained. The allyl ester **13** was also irradiated in benzene in order to trap intramolecularly (**14** in Scheme 3). The product isolated, however, was only benzothiophene **15** (20%). From these results, the direct dehydration mechanism of thiocarbonyl ylide **11** seems to be more attractive.

Pyrex-filtered irradiation of the series of methyl 2-arylthioacetoacetates **2a-l** in degassed benzene–methanol (1:1) solution generally gave the corresponding benzothiophene derivatives in fair yields as the sole product (Table 2). Similar results were observed for some α-arylthio-β-dicarbonyl compounds.[24]

In the case of **2h**, a regiospecific photocyclization was observed: only naphtho[2,1-b]thiophene **8** is formed with no trace of the [2,3-b] isomer **16**. The structure of **8** was supported by its ^{1}H NMR spectrum (Table 2) showing a characteristic downfield shift of the Me signal (δ 3.24) as a result of the deshielding effect of the proximate aromatic ring. The similar regiospecificity was reported for the photocyclization of 2-naphthyl vinyl sulfide.[4]

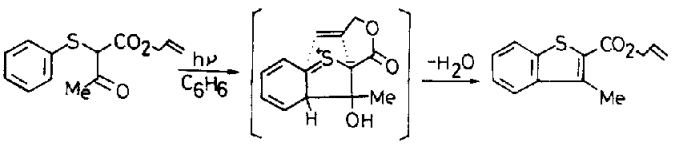


16

Compound **2j** was photoinert under the same conditions and the prolonged irradiation only led to the formation of a polymer. This result appears to bear relation to the unique spectral feature of **2j** (Table 1). The bimolecular H-bond like **2j''** makes the aromatic ring remote from the enol double bond. Therefore, no efficient interaction of two groups in the excited state can be expected for **2j**.

Irradiation of **2k** did not lead to detection of a cyclization product, but rather only to slow photopolymerization. This is interesting, because both **2i** and **2l** smoothly undergo photocyclization. The same factors controlling the regiochemistry of photocyclization of **2h** seem to play an important role in this reaction. When cyclization occurs at C(2), aromaticity in the adjacent ring is no longer retained and this would make the reaction very unfavorable.

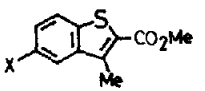
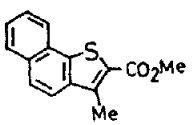
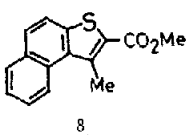
Photochemistry of some oxygen analogues have been investigated. Pyrex-filtered irradiation of methyl 2-phenoxyacetoacetate (**3a**) in degassed benzene–methanol

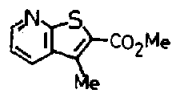
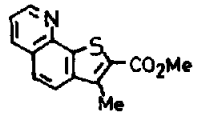
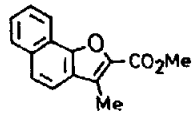
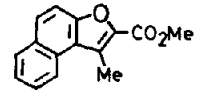


13 14 15

Scheme 3.

Table 2. Photocyclization of methyl 2-arylthio- and 2-aryloxyacetoacetates

substrate	product	irradiated time	yield, %[b]	mp, °C	IR, cm^{-1}	^{1}H NMR (δ, $CDCl_3$)[c] $COOCH_3$	CH_3	others	anal. calcd/found C	H
2a		8	66	104-105[d]	1695	3.91	2.77	7.30-7.92 (m,4H)	64.06	4.89
									64.13	4.94
	6a, X = H									
2b	6b, X = CH_3	6.5	61	89-90	1695	3.92	2.75	2.50(s,3H)	65.43	5.49
								7.2-7.8(m,3H)	65.60	5.55
2c	6c, X = OCH_3	6	57	93-95	1710	3.90	2.72	3.88(s,3H)	61.00	5.12
								7.09(dd,1H)[e]	61.22	5.19
								7.17(s,1H)		
								7.66(dd,1H)[f]		
2d	6d, X = F	9	56	131-132	1705	3.92	2.71	6.80-7.87 (m,3H)	58.92	4.05
									58.88	4.24
2e	6e, X = Cl	12	51	146-147	1705	3.93	2.73	7.45-7.85 (m,4H)	54.89	3.77
									54.69	4.03
2f	6f, X = Br	9	55	160-161	1710	3.90	2.70	7.46(ddd,1H)[g]	46.33	3.18
								7.64(dd,1H)[h]	45.93	3.55
								7.90 (m,1H)		
2g		7	64	159-161	1705	3.90	2.74	7.40-8.21 (m,6H)	70.29	4.72
	7								70.07	4.98
2h		11	56	127-128.5	1695	3.93	3.24	7.45-8.01 (m,5H)	70.29	4.72
	8							8.72(m,1H)	70.00	4.45

2i		9	50	1220124	1705	3.95	2.74	7.33(dd,1H)[i]	57.95	4.38	
	9								57.95	4.38	*
								8.08(dd,1H)[j]	57.90	4.42	
								8.67(dd,1H)[k]			
2j	none[o]	11							recovery		
2k	none[o]	3							recovery		
2l		6	53	138-139	1695	3.96	2.72	7.46(dd,1H)[l]	65.35	4.31	**
	10							7.73(m,2H)	65.35	4.56	
								8.20(dd,1H)[m]			
								8.93(dd,1H)[n]			
3a	none[o]	3							recovery		
3b		1.5	8	89-91	1705	4.04	2.68	7.50-8.15 (m,5H)	74.99	5.03	
	17[p]							8.50(m,1H)	74.76	5.26	
3c		1.5	10	122-124	1705	3.99	3.02	7.34-8.05 (m,5H)			
	18[q]							8.45(m,1H)			

[a] All photolyses were carried out in benzene-methanol (1:1) solution with a 100-W high pressure mercury lamp through a Pyrex filter. [b] Isolated yields. [c] All signals are singlets unless otherwise noted. [d] Lit.[18] mp 102.5-103°C. [e] J = 1.2 and 2.2 Hz. [f] J = 8.2 and 1.0 Hz. [g] J = 8.2, 1.6 and 0.4 Hz. [h] J = 8.2 and 0.9 Hz. [i] J = 8.0 and 4.5 Hz. [j] J = 8.0 and 1.5 Hz. [k] J = 4.5 and 1.5 Hz. [l] J = 8.4 and 4.5 Hz. [m] J = 8.4 and 1.5 Hz. [n] J = 4.5 and 1.5 Hz. [o] See text. [p] MS m/e (rel intensity) 240 (M^+, 100), 209 (59). [q] MS m/e (rel intensity) 240 (M^+, 100), 209 (52). * anal. N(calcd/found) = (6.76/6.98). ** anal. N(calcd/found) = (5.44/5.40).

(1 : 1) resulted in the recovery of the starting material along with the formation of a polymeric substance and a small amount of phenol. Irradiation with a quartz filter only led to increase of polymer formation. Pyrex-filtered irradiation of naphthyl derivatives **3b** and **3c** under the same conditions afforded naphthofurans **17** and **18**, respectively, in rather low yield (Table 2). Regiospecificity of photocyclization of **3c** is analogous to that of **2h** and the product is only naphtho[2,1-b]furan **18** which shows the similar down-field shift of Me signal in the ^{1}H NMR spectrum (Table 2).

Photocyclization of aryl vinyl ethers is well documented.[8,25] The reaction seems to proceed similarly via carbonyl ylide intermediate (ex, **11** (X = O)). The dihydrofuran derivatives[8] (ex, **12** (X = O)) were again not detected. The low efficiency of photocyclization of 2-aryloxyacetoacetates compared with that of 2-arylthioacetoacetates can be attributed to its poor enolization ability (Table 1).

EXPERIMENTAL

General. M.ps were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed with Perkin–Elmer 240 B elemental analyzer. UV spectra were determined with a Hitachi spectrophotometer (Model 200-10). ^{1}H NMR spectra were taken with a JEOL C-60-HL spectrometer and with a JEOL FX 60 FT NMR spectrometer, TMS was used as an internal standard. IR spectra were taken with a JASCO IRA-1 spectrometer. Mass spectra were obtained with a Hitachi RMS-mass spectrometer at 70 eV.

Methyl 2-phenylthioacetoacetate (**2a**)

General procedure for preparation of methyl 2-arylthioacetoacetates. Et_3N (1.59 g, 15.7 mmol) was added dropwise to a stirred soln of **1**[26] (2.38 g, 15.0 mmol) and thiophenol (1.65 g, 15.0 mmol) in CH_2Cl_2 (25 ml) at 0° under N_2. The mixture was stirred overnight at room temp. At the end of this time n-hexane (150 ml) was added and the resulting mixture was washed with water (3 × 50 ml). The organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The yellow oil obtained was chromatographed on a silica gel column using n-hexane-EtOAc (10:1) to give **2a** (3.15 g, 94%) as colorless oil, bp 115–120° (1.0 mm); IR (neat) 3080–2700 (br), 1630, 1595, 1485, 1450, 1345 and 1260 cm^{-1}; UV (MeOH) 248 (ε 17840) and 292 nm (ε 2048, sh). The ^{1}H NMR data are summarized in Table 1. (Found: C, 58.78; H, 5.23. $C_{11}H_{12}O_3S$ requires: C, 58.91; H, 5.39%). Compounds **2b–2k** were prepared from **1** and arylmercaptanes similarly as **2a**. The yields and physical data of those compounds were summarized in Tables 2 and 3.

Methyl 2-(8-quinolylthio)acetoacetate (**2l**). The tin salt of 8-quinolinethiol was prepared from 8-quinolinesulfonyl chloride according to the method of Badger and Buttery.[11] The salt (1.55 g, 3.53 mmol) and **1** (1.06 g, 7.1 mmol) was dissolved in CH_2Cl_2-DMF (3:1) (20 ml) and the resulting mixture was stirred

Table 3. Preparation of 2-substituted methyl acetoacetates

product	yield(%)	mp, °C	IR, cm^{-1}	anal. calcd/found C	H	N
2a	94		3080 2700(br) 1630	58.95	5.39	
			1595 1485 1345	58.78	5.23	
2b	93	73-74	3040 2720 1590	60.48	5.92	
			1435 1335 1250	60.43	5.90	
2c	98		1720 1585 1490	56.68	5.55	
			1435 1330 1240	56.65	5.58	
2d	98		3040-2680 1590	54.54	4.58	
			1490 1445 1380	54.43	4.52	
			1340			
2e	83	50-52	3040-2640 1580	51.07	4.29	
			1435 1330 1240	50.81	4.23	
2f	90	61-63	3020-2680 1585	43.58	3.66	
			1440 1370 1320	43.56	3.68	
2g	86	105-107	3080-2680 1595	65.67	5.14	
			1440 1335	65.79	5.23	
2h	78	142-144	3420 1620 1595	65.67	5.14	
			1505 1335	65.81	5.38	
2j	87	45-47	3080-2680 1575	53.32	4.92	6.22
			1440 1425	53.37	4.89	6.15
2k			3060-2640 1715	61.08	4.76	5.09
			1590 1445 1340	60.93	4.53	4.98
			1255			
2l	47	137-138	1615 1590 1440	61.08	4.76	5.09
			1325 1240	60.04	4.74	5.02
3a	22		1745 1725 1650	63.45	5.81	
			1590 1485 1435	63.42	5.84	
3b	37		3065 1750 1725	69.76	5.46	
			1655 1580	69.46	5.49	
3c	33		3080 1765 1735	69.76	5.46	
			1630 1615 1435	69.70	5.52	

overnight at room temp. The insoluble salts were removed by filtration and filtrate was evaporated under reduced pressure. The residue was chromatographed on a silica gel column using n-hexane–EtOAc (3:1) and recrystallized from ether–CH_2Cl_2 to give **21** as colorless crystals (455 mg, 47%), m.p. 137–138°; IR (KBr) 1615, 1590, 1440, 1325 and 1240 cm^{-1}. The ^1H NMR data are listed in Table 1. (Found: C, 60.84; H, 4.74; N, 5.02. $C_{14}H_{13}NO_3S$ requires: C, 61.08; H, 4.76; N, 5.09%).

Methyl 2-phenoxyacetoacetate (**3a**)

General procedure for preparation of 2-aryloxyacetoacetates. A soln of phenol (941 mg, 10 mmol) in dry THF (4 ml) was carefully added at 0° to a stirred suspension of NaH (60% in oil, 400 mg, 10 mmol) in THF (5 ml) under Ar. After the mixture was stirred at room temp for 1 hr, tetramethylethylenediamine (1.16 g, 10 mmol) and **1** (1.50 g, 10 mmol) were added. The resulting soln was heated to reflux for 4 hr. At the end of this time water (15 ml) was added and the resulting mixture was extracted with CH_2Cl_2 (3 × 30 ml). The combined organic layer was washed with brine, dried over $NaSO_4$, and evaporated under reduced pressure. The brown residual oil was chromatographed on a silica gel column using n-hexane–$CHCl_3$ (1:1) to give **3a** as colorless viscous oil (451 mg, 22%); IR (neat) 1745, 1725, 1650, 1590, 1485, 1435, 1350, 1260 and 1200 cm^{-1}. The ^1H NMR data are summarized in Table 1. (Found: C, 63.42; H, 5.84. $C_{11}H_{12}O_4$ requires: C, 63.45; H, 5.81%). Compounds **3b–3c** were prepared from **1** and arylmercaptanes similarly as **3a**. The yields and physical data of those compounds were summarized in Tables 1 and 3.

Irradiation of **2a**

General photochemcial procedure. A soln of **2a** (500 mg, 2.23 mmol) in benzene–MeOH (1:1, 120 ml) was placed in the preparative photoreactor and Ar was passed into the soln for 15 min prior to and during irradiation. The soln was irradiated with a Ushio 100-W high pressure mercury lamp placed in a water -cooled Pyrex well. After 8 hr, the solvent was evaporated under reduced pressure and the residue was chromatographed on a short silica gel column using n-hexane–EtOAc (20:1) in order to remove the polymeric substances. The colorless solid obtained was recrystallized from n-hexane–ether to give **6a** (305 g, 66%) as colorless needles, m.p. 104–105° (Lit.[18] m.p. 102.5–103°). IR and ^1H NMR data are summarized in Table 2. Compounds **2b–3c** were also irradiated as above. The results were summarized in Table 2.

Irradiation of **2a** (300 mg, 1.34 mmol) in each 100 ml of benzene, acetone, acetonitrile, chloroform and methanol under the same conditions followed by the similar work-up gave **6a** in 29%, 21%, 19%, 21% and 41% yields, respectively.

Anhyd Na_2CO_3 (150 mg) was added to a soln of **2a** (360 mg, 1.6 mmol) in n-hexane (100 ml) and the resulting mixture was irradiated for 4 hr under vigorous stirring. The insoluble base was filtered off and the filtrate was evaporated under reduced pressure. Chromatography and crystallization from n-hexane gave **6a** (95 mg, 29%).

Irradiation of **2h** *in the presence of N-phenylmaleimide.* A soln of **2h** (150 mg, 0.55 mmol) and N-phenylmaleimide (190 mg, 1.1 mmol) in benzene (100 ml) was irradiated for 3 hr under Ar. Evaporation and column chromatography on silica gel using hexane–EtOAc (10:1) gave **8** (41 mg, 29%) and unreacted N-phenylmaleimide (145 mg, 76%) in the order of elution.

Allyl 2-phenylthioacetoacetate (**13**). A soln of **2a** (500 mg, 2.23 mmol) in allyl alcohol (5 ml) containing 2 drops H_2SO_4 was heated under reflux for 10 hr. At the end of this time solid K_2CO_3 and ether (30 ml) were added and the resulting mixture was washed with $NaHCO_3$aq and water, dried over $NaSO_4$, and evaporated, The residue was chromatographed on a silica gel column using n-hexane–EtOAc (12:1) to give **13** (250 mg, 45%) as colorless oil; IR (neat) 3080–2640 (br), 1620, 1585, 1380, 1325 and 1240 cm^{-1}; NMR ($CDCl_3$) δ 2.32 (s, 3H), 4.59 (dm, J = 5.0 Hz, 2H), 4.90–5.32 (m, 2H), 5.46–6.10 (m, 1H), 6.90–7.35 (m, 5H), 13.62 (s, 1H). (Found: C, 62.53; H, 5.71. $C_{13}H_{14}O_3S$ requires: C, 62.38; H, 5.64%).

Irradiation of **13**. A soln of **13** (120 mg, 0.48 mmol) in benzene (80 ml) was irradiated for 4 hr. Evaporation and column chromatography using hexane–EtOAc (40:1) afforded **15** (25 mg, 22%) as colorless oil, b.p. 120–125° (1.0 mm); IR (neat) 1695, 1270, 1235, 1105 and 1050 cm^{-1}; NMR ($CDCl_3$) δ 2.76 (s, 3H), 4.79 (dd, J = 5.2 and 1.2 Hz, 2H), 5.12–5.65 (m, 2H), 5.72–6.30 (m, 1H), 7.25–7.88 (m, 4H). (Found: C, 67.10; H, 5.33. $C_{13}H_{12}O_2S$ requires: C, 67.22; H, 5.21%).

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