# Reactions Leading to 1,2-Dibenzoylethanes: The Dehalogenation of Phenacyl Bromide and the Photolysis of Methyl Phenacyl Sulfoxide

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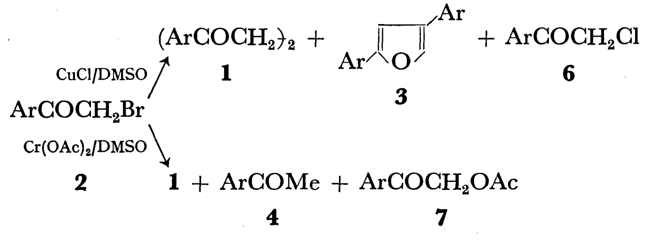
The dehalogenation of phenacyl bromide by means of lower-oxidation-state metallic ions complexed by DMSO gives 1,2-dibenzoylethane. The by-products are 2,4-diphenylfuran and phenacyl chloride in the presence of Cu(I) chloride, whereas acetophenone and ω-acetoxyacetophenone are produced in the reaction with Cr(II) acetate. Treatment with $K_3Co(CN)_5$/DMSO gives 1,2-dibenzoylethane and acetophenone. The second title reaction consists of the photolysis of methyl phenacyl sulfoxides, the isolated by-products being acetophenones and methyl methanethiolsulfonate. The product distribution is strongly affected by the pH of the reaction mixture and also by the benzene-ring substituents.

Few reactions are known with respect to the formation of 1,2-dibenzoylethane (**1**) *via* the dehalogenation of phenacyl halides (**2**) or the recombination of phenacyl radicals. The treatment of phenacyl bromide (**2a**) with nickel carbonyl gives 1,2-dibenzoylethane (**1a**) in THF, whereas 2,4-diphenylfuran (**3a**) is the sole product in the DMF solvent.[1] The photolysis of dimethylphenacylsulfonium bromide in an aqueous solution gives **1a** besides **2a** and acetophenone (**4a**).[2] We now wish to record two independent reactions producing **1a**: the dehalogenation of phenacyl bromide with lower-oxidation-state metal salts dissolved in DMSO and the photolysis of methyl phenacyl sulfoxide (**5a**).[3]

*Dehalogenation of Phenacyl Halide.* Complexed metal salts of the lower oxidation state effectively dehalogenate organic halides.[4,5] In continuation of previous studies along this line,[6] we have now examined the reaction of phenacyl bromide with Cu(I) chloride, Cr(II) acetate, and $K_3Co(CN)_5$, all dissolved in DMSO: we thus obtained **1a** in varying yields, along with by-products, as is shown in Scheme 1 and Table 1.



a: Ar=Ph, b: Ar=$p$-$BrC_6H_4$-

Scheme 1

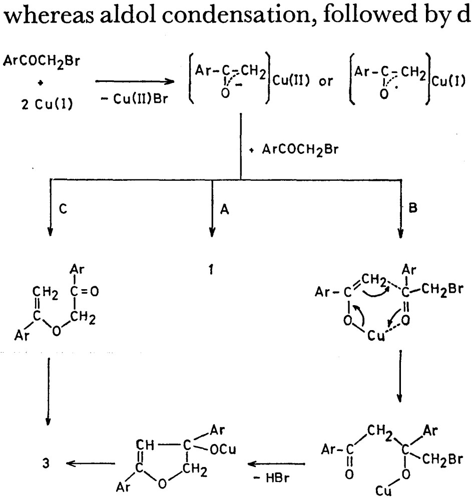
TABLE 1. REACTION OF $ArCOCH_2Br$ WITH CuCl, $Cr(OAc)_2$, OR $K_3Co(CN)_5$ IN DMSO[a)]

| Components | Reaction time (hr) | Products yield (%)[b)] | | | | |
|---|---|---|---|---|---|---|
| | | 1 | 3 | 4 | 6 | 7 |
| **2a**+CuCl | 18.5 | 13 | 14 | | 39 | |
| **2b**+CuCl | 38.5 | 11 | 13 | | 43 | |
| **2a**+$Cr(OAc)_2$ | 12.5 | 28 | | — | | 43 |
| **2b**+$Cr(OAc)_2$ | 23 | 16 | | 32 | | 18 |
| **2a**+$K_3Co(CN)_5$ | 24 | 7 | | 50 | | |
| **2b**+$K_3Co(CN)_5$ | 17 | 25 | | 40 | | |

a) Each reaction was carried out at room temperature (CuCl and $Cr(OAc)_2$) and 80—90°C ($K_3Co(CN)_5$) in $N_2$ atmosphere with 1 M DMSO solution or of the salt with Br/metal ratio of 1:2.5.

b) The isolation yields were based on **2**. The recovery was not considered.

The formation of 2,4-diarylfurans (**3a**, **3b**) in the Cu(I) reaction is parallel to previous observations made of the reactions of α-haloketones with nickel(0) tetracarbonyl,[1] metallic magnesium,[7] or zinc.[8] Analogously with these reactions, we may account for the route to **3a**, and **3b** as in Scheme 2, where the intermediacy of Cu(I) enolate is postulated.[7,8] The Wurtz-type condensation of this enolate with **2** (Route A) or, alternatively, the recombination of phenacyl radicals gives **1**, whereas aldol condensation, followed by dehydro-



Scheme 2.

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Table 2. Photolysis of $ArCOCH_2SOMe$ (5)[a)]

| | Ar | Solvent | Reaction time (hr) | Products | | | |
|---|---|---|---|---|---|---|---|
| | | | | **1** | **4** | **8** | ArCOOH |
| **5a** | Ph | EtOH | 5 | 38 | 49 | 8 | — |
| **5a** | Ph | EtOH[b)] | 5 | 20 | 46 | 13 | — |
| **5a** | Ph | *t*-BuOH | 4 | 72 | 23 | 52 | — |
| **5a** | Ph | *i*-PrOH | 8 | 24 | 20 | 8 | — |
| **5a** | Ph | PhH | 8 | 62 | trace | 61 | — |
| **5a** | Ph | $EtOH(H_2SO_4)$[c)] | 5 | 12 | 87 | 8 | — |
| **5a** | Ph | EtOH(NaOH)[d)] | 5 | 54 | 27 | — | 17 |
| **5b** | $p$-$BrC_6H_4$ | EtOH | 5 | 19 | 70 | 10 | — |
| **5c** | $p$-$ClC_6H_4$ | EtOH | 5 | 33 | 60 | 12 | 4 |
| **5c** | $p$-$ClC_6H_4$ | $EtOH$-$H_2O$[e)] | 5 | 30 | 6 | 4 | — |
| **5c** | $p$-$ClC_6H_4$ | $EtOH(H_2SO_4)$[c)] | 5 | trace | 71 | trace | — |
| **5c** | $p$-$ClC_6H_4$ | EtOH(NaOH)[d)] | 5 | 70 | 15 | — | 13 |
| **5d** | $p$-$MeC_6H_4$ | EtOH | 6 | 25 | 30 | — | — |
| **5e** | $p$-$MeOC_6H_4$ | EtOH | 2 | trace | 88 | trace | — |
| **5e** | $p$-$MeOC_6H_4$ | $EtOH(H_2SO_4)$[c)] | 2 | — | 95 | trace | — |
| **5e** | $p$-$MeOC_6H_4$ | EtOH(NaOH)[d)] | 2 | 32 | 28 | — | 20 |
| **5f** | $p$-$Me_2NC_6H_4$ | EtOH[f)] | 46 | 41 | 34 | — | — |
| **5g** | $\alpha$-$C_{10}H_7$ | EtOH | 70 | — | 63 | — | — |

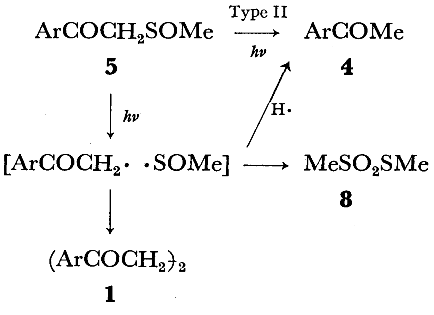
a) Irradiation was performed on 0.1 M solutions with an external 200W high pressure mercury lamp through a Pyrex filter at room temperature under nitrogen atmosphere.
b) Irradiation under oxygen atmosphere.
c) A trace of concentrated $H_2SO_4$ was added to adjust the pH of the media at 5—6 on a test paper.
d) A trace of 10% NaOH (EtOH) was added to adjust the pH of the media at 8—9.
e) $EtOH:H_2O=2:1$ (volume ratio). A by product, $p$-$ClC_6H_4COCH_2SO_2Me$ (18%) was obtained.
f) A by product, $p$-$Me_2N$-$C_6H_4COCH_2OH$ (20%) was obtained.

bromination (Route B), produces the furans **3**. Schematically, the possibility of Route C cannot be excluded. The anhydrous Cr(II) acetate/DMSO system is apparently less selective than the previously-recorded Cr(II) sulfate/aqueous DMF system,[4c)] which produces **4** almost quantitatively. The complete absence of aldol condensation in the Cr(II) reaction may be ascribed to the higher covalency of the chromium-phenacyl bond than that of copper enolate. The ligand-ligand reaction leading to **7** prevails in this case.

Few organic reactions have been recorded to occur under the participation of $K_3Co(CN)_5$.[9—12)] The reaction with **2** is mainly reduction to **4** in DMSO. Smaller yields of **1** were obtained.

*Photolysis of Phenacyl Sulfoxides (5).* The irradiation of $\beta$-keto sulfones[13)] or $\beta$-keto sulfides[14)] ($RCOCH_2$-$X$-$CH_2R'$, $X=SO_2$ or S) gives $RCOCH_3$ ketones. The reaction of the sulfides is supposed to proceed *via* the Norrish type-II route, whereas that of sulfones has been claimed to involve the homolysis of the C-S bond, followed by hydrogen abstraction by the $RCOCH_2\cdot$ radicals.

The photochemistry of the $\beta$-keto sulfoxides[15,16)] now readily available has apparently not been described. We will report the formation of **1** and **4** in the photolysis of phenacyl sulfoxides, **5**, mainly in ethanol (Scheme 3), as well as the effects of the pH values of the reacting media and those of aromatic substituents. The results are summarized in Table 2.



Scheme 3

At the initial stage of this investigation we experienced difficulties in securing reproducible experimental data. Soon it was found that the product distribution is quite sensitive to the pH of the reaction media. Table 2 contains the effect of added acids and bases. Slightly basic conditions favor the yields of dibenzoylethanes, **1**, whereas acetophenones, **4**, are mainly produced under acidic conditions. This effect may be ascribed to the amphoteric character of the phenacyl sulfoxide, that is, to the methylene acidity and the SO

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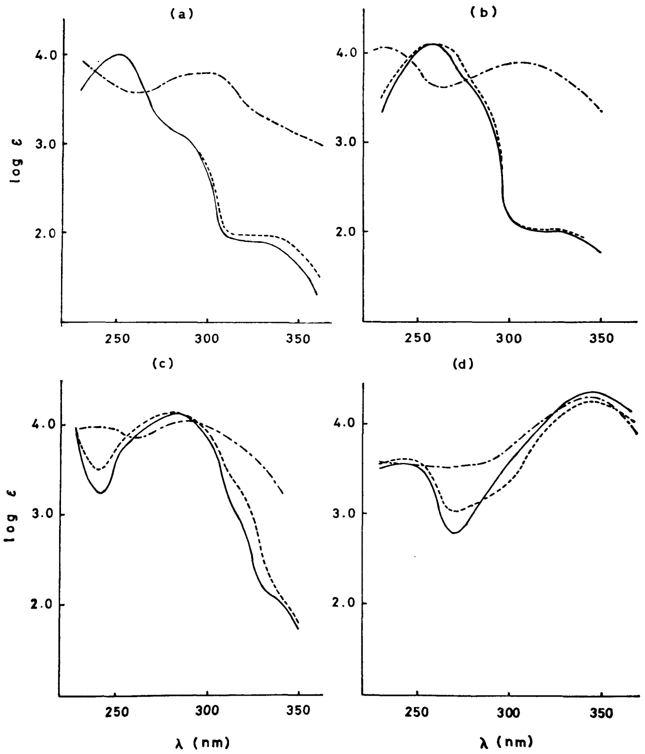

Fig. 1. UV spectra of β-keto sulfoxides in ethanol (——), ethanol-$H_2SO_4$(------), and ethanol-NaOH (-·-·).
(a) $PhCOCH_2SOMe$ (**5a**); (b) p-$ClC_6H_4COCH_2SOMe$ (**5c**); (c) p-$MeOC_6H_4COCH_2SOMe$ (**5e**); (d) p-$Me_2NC_6H_4COCH_2SOMe$ (**5f**).

oxygen basicity (*vide infra*). Aromatic substituents also influenced the product distribution; the *p*-dimethylamino group strongly increased the yield of **1**, while *p*-methoxy and *p*-halogen substituents favored **4**. In *t*-butyl alcohol or benzene, **5a** gave **1a** mainly.

The UV absorptions of the reacting mixtures are given in Fig. 1. The bathochromic and hyperchromic shift of longer wavelength ($n$-$\pi^*$) absorptions was observed under basic conditions, the presence of a trace of acid did not change the spectra appreciably. The spectra of the *p*-dimethylamino derivative, **5f**, showed little dependence on the pH and remarkably resembled ot the spectra of **5a**, **5c**, and **5e** under basic conditions. The relationship between the product distribution and the spectral change has not yet been clearly explained. The photolysis appears to involve initial homolysis of the phenacyl-SO bond. The $ArCOCH_2\cdot$ radicals then dimerize to **1** or, alternatively, abstract hydrogen from the solvent to give **4**. Presumably, smaller photoquanta under basic conditions give less energetic $ArCOCH_2\cdot$ radicals, which easily dimerize. The absence of the removable solvent hydrogen also favors the formation of **1**. The counter radicals, $\cdot SOMe$, dimerize to give methyl methanethiolsulfonate (**8**), which has been isolated as is shown in Table 2.

## Experimental

All the mps are uncorrected. The microanalyses were performed at the Elemental Analyses Center of Kyoto University and by Mrs. K. Fujimoto of this Department. The NMR spectra were taken on a 60 MHz instrument (JEOL C-60H spectrometer) in deuteriochloroform or carbon tetrachloride with tetramethylsilane as the internal standard. The UV spectra were obtained on a Shimadzu MPS-50L spectrometer.

Unless otherwise stated, irradiation was effected externally by means of a 200-W high pressure mercury lamp under a nitrogen atmosphere at room temperature.

Commercial Cu(I) chloride was used without purification. Cr(II) acetate and $K_3Co(CN)_5$ were prepared according to the methods shown in the literature.[12,17] The β-keto sulfoxides were synthesized by the Corey method.[15] The NMR, IR, and microanalyses of novel ones are given below.

*Methyl* p-*chlorophenacyl sulfoxide (5c)* showed a mp of 128°C. IR (Nujol): 1670 cm$^{-1}$ ($\nu_{C=O}$), 1030 cm$^{-1}$ ($\nu_{SO}$). NMR ($CDCl_3$): δ 2.80 (s, 3H, Me), 4.40 (s, 2H, $-CH_2-$), and 7.35—8.15 (two d, 4H, aromatic protons).

Found: C, 50.2; H, 4.2%. Calcd for $C_9H_9ClO_2S$: C, 49.9; H, 4.2%.

*Methyl* p-N,N-*dimethylaminophenacyl sulfoxide (5f)* showed a mp of 144—145°C. IR (Nujol): 1600 cm$^{-1}$ ($\nu_{C=O}$), 1020 cm$^{-1}$ ($\nu_{SO}$). NMR ($CDCl_3$): δ 2.74 (s, 3H, -SOMe), 3.10 3.10 (s, 6H, $Me_2N$), 4.02—4.63 (two d, 2H, $-CH_2-$), and 6.59—7.93 (two d, 4H, aromatic protons).

Found: C, 58.6; H, 6.6%. Calcd for $C_{11}H_{15}NO_2S$: C, 58.6; H, 6.7%.

*Reaction of Phenacyl Bromide (2a) with Cu(I) Chloride.* In a $N_2$ atmosphere, Cu(I) chloride (1.5 g, 15 mmol) was dissolved in freshly-distilled DMSO (30 m*l*) (over $CaH_2$). To this, a solution of **2a** (1.2 g, 6.0 mmol) in DMSO (10 m*l*) was added. The reaction mixture was stirred for 18.5 hr at room temperature, treated with water and extracted with ether. The extract was then washed with water, dried ($Na_2SO_4$), and concentrated *in vacuo*. Chromatography on a silica-gel column gave 1,2-dibenzoylethane (**1a**) (0.09 g, 13%), 2,4-diphenylfuran (**3a**) (0.09 g, 14%), and phenacyl chloride (**6a**) (0.36 g, 39%). The **1a** product showed a mp of 148—150°C (lit.[1] 145°C) and was identical with an authentic sample. IR (Nujol): 1675 cm$^{-1}$ ($\nu_{C=O}$). NMR ($CDCl_3$): δ 3.47 (s, 4H, $-CH_2-$) and 7.35—8.40 (m, 10H, aromatic protons). The **3a** product showed a mp of 111°C (lit.[18] 111°C). IR (Nujol): 1538 and 910 cm$^{-1}$ (furan ring). NMR ($CCl_4$): δ 6.82 (s, 1H, proton of the furan ring at the C-3 position) and 7.15—7.65 (m, 11H, protons of the benzene ring and furan ring at the C-5 position). The **6a** product showd a mp of 57—58°C (lit.[19] 58°C), and its structure was supported by NMR and IR.

*Reaction of* p-*Bromophenacyl Bromide (2b) with Cu(I) Chloride.* A solution of Cu(I) chloride (0.89 g, 9.0 mmol) in DMSO (30 m*l*) was prepared under $N_2$. To this, a solution of **2b** (0.99 g, 3.6 mmol) in DMSO (10 m*l*) was added and the mixture was stirred at room temperature for 38.5 hr. Chromatography on a silica-gel column gave **1b** (0.08 g, 11%), **3b** (0.09 g, 13%), and **6b** (0.36 g, 43%). The **1b** product showed a mp of 180°C (lit.[1] 180—181°C). IR (Nujol): 1670 cm$^{-1}$ ($\nu_{C=O}$). NMR ($CDCl_3$): δ 3.43 (s, 4H, $-CH_2-$) and 7.54—7.98 (m, 8H, protons of the aromatic ring). The **3b** product showed a mp of 160°C. IR (Nujol): 1539 and 912 cm$^{-1}$ (furan ring). NMR ($CDCl_3$): δ 6.90 (s, 1H, proton of the furan ring at the C-3 position) and

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7.40—7.73 (m, 9H, protons of the aromatic ring and the furan ring at the C-5 position). The **6b** product showed a mp of 116—118°C (from ethanol) (lit.[20] 117—118°C).

*Reaction of 2a with Cr(II) Acetate.* Under N$_2$, Cr(II) acetate (1.5 g, 8.8 mmol) was dissolved in DMSO (50 m*l*) so to give *ca.* 0.18 M solution. To this, a solution of **2a** (0.70 g, 3.5 mmol) in DMSO (10 m*l*) was added and the mixture was stirred at room temperature for 12.5 hr. Chromatography on a silica-gel column gave **1a** (0.12 g, 28%), ω-acetoxyacetophenone (**7a**) (0.27 g, 43%). The **7a** product showed a mp of 47—49°C (lit.[21] 49°C); its structure was supported by the IR and NMR.

*Reaction of 2b with Cr(II) Acetate.* The **2a** halide (2.23 g, 8.0 mmol) in DMSO (10 m*l*) was treated with a solution of Cr(II) acetate (3.40 g, 20 mmol) in DMSO (100 m*l*) at room temperature for 23 hr to afford **1b** (0.25 g 16%), **4b** (0.51 g, 32%), and **7b** (0.37 g, 18%). The **7b** product showed a mp of 84—85°C (lit.[22] 85°C).

*Reaction of 2a with K$_3$Co(CN)$_5$.* A solution of the cyanocobalt(II) complex was prepared under N$_2$ from potassium cyanide (9.75 g, 150 mmol) and Co(II) chloride (3.25 g, 25 mmol) in DMSO (50 m*l*). To this, a solution of **2a** (2.0 g, 10 mmol) in DMSO (5 m*l*) was added, and the mixture was stirred at 80—90°C for 24 hr. A subsequent work-up gave **1a** (0.08 g, 7%) and **4a** (0.60 g, 50%).

*Reaction of 2b with K$_3$Co(CN)$_5$.* To a solution of the cobalt complex prepared from potassium cyanide (4.88 g, 75 mmol) and Co(II) chloride (1.63 g, 13 mmol) in DMSO (50 m*l*), a solution of **2b** (1.39 g, 5.0 mmol) in DMSO (10 m*l*) was added, after which the mixture was stirred at 80—90°C for 17 hr. A subsequent work-up gave **1b** (0.25 g, 25%) and **4b** (0.40 g, 40%).

*Photolysis of Methyl Phenacyl Sulfoxide (5a).* Sulfoxide **5a** (0.182 g, 1 mmol) was dissolved in ethanol (10 m*l*) and degassed under vacuum at −70°C on a dry-ice bath. This was then irradiated by means of high-pressure mercury lamp for 5 hr. After the irradiation, the ethanol was removed *in vacuo* and the residue was chromatographed on a silica-gel column. 1,2-Dibenzoylethane (**1a**) (0.045 g, 38%), acetophenone (**4a**) (0.06 g, 49%), and methyl methanethiolsulfonate (**8**) (0.005 g, 8%) were obtained. The **8** product was identical with an authentic sample.

The photolyses of **5b**—**5g** were carried out under similar conditions. The results are summarized in Table 2. All the acetophenone derivatives were identical with authentic samples. The **1c**, **1d**, and **1e** products showed mps of 151°C (lit.[23] 151°C), 158—159°C (lit.[24] 159°C) and 154—155°C (lit.[25] 154°C) respectively, their structures were supported by IR and NMR. The **1f** product did not melt below 220°C. IR (Nujol): 1595 cm$^{-1}$ ($\nu_{C=O}$). NMR (CDCl$_3$): $\delta$ 3.03 (s, 12H, Me$_2$N), 3.33 (s, 4H, -CH$_2$CH$_2$-), and 6.45—8.10 (two d, 8H, aromatic protons). Microanlyses were carried out without purification, as **1f** is difficult to purify in conventional ways.

Found: C, 73.2; H, 7.5; N, 8.4%. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.0; H, 7.5; N, 8.6%.

A by-product, ω-hydroxy-*p*-*N*,*N*-dimethylaminoacetophenone, showed a mp of 155°C. NMR (CDCl$_3$): $\delta$ 3.10 (s, 6H, -NMe$_2$), 4.74 (s, 2H, -CH$_2$-), 7.35 (s, 1H, OH) and 6.55—7.97 (two d, 4H, aromatic protons). MS: 179 (M$^+$).

Found: C, 67.3; H, 7.2; N, 7.6%. Calcd for $C_{10}H_{13}NO_2$: C, 67.0; H, 7.3; N, 7.8%.

*Photolysis of 5a in the Presence of Sulfuric Acid.* The sulfoxide, **5a** (0.182 g, 1 mmol), was dissolved in ethanol (10 m*l*). A solution of sulfuric acid in ethanol was then added, drop by drop, so to give a solution of pH 5—6 (pH test paper). This solution was degassed and then irradiated under N$_2$ for 5 hr. The products were isolated and identified as has been described above. The photoreactions of **5c** and **5e** was carried out under similar conditions. The results are summarized in Table 2.

*Photolysis of 5a in the Presence of Sodium Hydroxide.* The sulfoxide, **5a** (0.182 g, 1 mmol), was dissolved in ethanol (10 m*l*). A solution of sodium hydroxide in ethanol was then added, drop by drop, so to give a solution of pH 8—9. This solution was irradiated under N$_2$ for 5 hr and the products were confirmed as has been described above. The results are summarized in Table 2.

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