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THE PREPARATION OF 1,4-DICARBONYL COMPOUNDS BY PHOTOREACTION OF KETONES IN THE PRESENCE OF OXIDANTS

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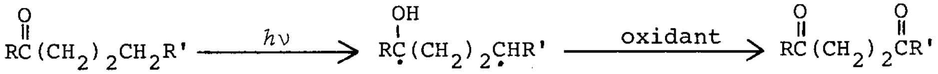
Abstract: Phenyl alkyl ketones were photo-irradiated in the presence of Cr(VI) or Mn(VII) oxidants to yield 1,4-dicarbonyl compounds regiospecifically while 2-octanone gave a regioisomeric mixture of 2,5-, 2,6-, and 2,7-octadiones.

Several substrates have been known to trap the biradicals generated in the Norrish type II reaction of ketones, introducing the new substituents at γ-positions of the original carbonyl groups such as a deuterium with a deuterated thiol,$^{1)}$ an alkyl group with an olefin,$^{2)}$ and a selenyl group with a selenoketone.$^{3)}$ Although oxygen has been reported to give a γ-hydroperoxyketone,$^{4)}$ the introduction of a carbonyl group with oxidants has not been so far found to our knowledge.$^{5)}$ We wish here to report an one-step synthesis of 1,4-dicarbonyl compounds which is brought about by oxidation of 1,4-diradical intermediates generated from ketones under the photo-irradiation.



$$\overset{\overset{O}{\|}}{R C}(CH_2)_2CH_2R' \xrightarrow{h\nu} \overset{\overset{OH}{|}}{R\dot{C}}(CH_2)_2\dot{C}HR' \xrightarrow{\text{oxidant}} \overset{\overset{O}{\|}}{R C}(CH_2)_2\overset{\overset{O}{\|}}{C}R'$$

Photoreaction of hexanophenone (1) was performed in aq.CH_3CN in the presence of oxidants under a nitrogen atmosphere using a high-pressure Hg lamp to afford 1-phenylhexane-1,4-dione (2), the expected 1,4-dicarbonyl compound, although, in the case of $K_2Cr_2O_7$ or $KMnO_4$ under a neutral condition, the conversion was very low possibly because of appearance of a deposit around a reaction vessel. An aq.acetonitrle solution containing 1, hydrochloric acid and an oxidant, in turn, was irradiated under a nitrogen atmosphere with a low-

Table 1. Photoreaction of 1 in the presence of oxidants

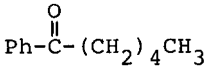
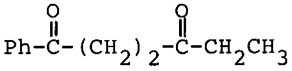
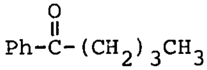
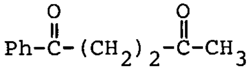
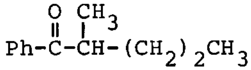
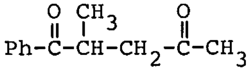
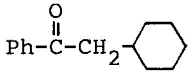
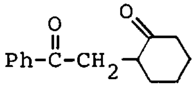
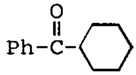
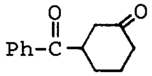
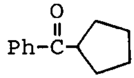
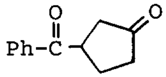
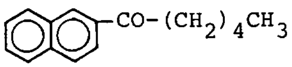
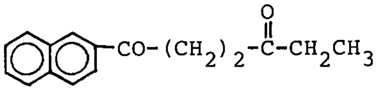
Run[a]	Oxidant	Hg lamp	1/Oxidant mole ratio	HCl/Oxidant mole ratio	Conversion[b] (%)	Yield(%)[b,c] 2	Yield(%)[b,c] $PhCOCH_3$
1	$K_2Cr_2O_7$	high	0.83	0	17	18	29
2	$K_2Cr_2O_7$	high	0.56	5.2	100	15	14
3	$KMnO_4$	high	0.67	0	10	60	trace
4	$KMnO_4$	high	0.50	4.0	10	trace	42
5	$NaIO_4$	high	0.77	0	100	trace	6
6	$K_2Cr_2O_7$	low	0.28	4.6	24	53	15
7	$K_2Cr_2O_7$	low	0.56	4.5	97	39	22
8	$K_2Cr_2O_7$	low	0.53	2.2	85	82	9
9[d]	$K_2Cr_2O_7$	low	1.1	2.2	97	49	36
10	$KMnO_4$	low	0.50	1.7	45	71	19
11	$KMnO_4$	low	0.50	4.0	17	66	25
12	CrO_3	low	0.48	1.8	100	64	35
13	K_2CrO_4	low	0.50	1.9	77	40	40

[a] Irradiation time=24 hr. [b] Determined by VPC. [c] Based on 1 consumed.

[d] Irradiation time=17.5 hr.

pressure Hg lamp. In the case of $KMnO_4$ as an oxidant, although 2 was produced in moderate yields, conversions of 1 were low possibly because, at low acid concentration, light transmission decreases due to appearance of the deposit around a reaction vessel under photo-irradiation and, at high acid concentration, $KMnO_4$ may operate strongly as a quencher (Table 1, run 10 and 11). $K_2Cr_2O_7$ was proved to be the better oxidant for the production of 2 than $KMnO_4$. The effects of the concentrations of $K_2Cr_2O_7$ and HCl on the yield of 2 were investigated to reveal that the increase of the former and the decrease of the latter bring about the elevation of the yield of 2 under the reduction of the yield of acetophenone, the normal Norrish type II product, although the conversion of 1 is diminished (Table 1, runs from 6 to 9). Thus, we decided the mole ratios of 1 and HCl to $K_2Cr_2O_7$ suitable for the formation of 2 as 0.5 and 2.2, respectively (Table 1, run 8). K_2CrO_4 and CrO_3 as Cr(VI) oxidants appeared to afford 2 comparably with $K_2Cr_2O_7$. These results under irradiation with high- and low-pressure Hg lamps are shown in Table 1. Some aryl ketones were irradiated under the same condition as that in run 8 of Table 1 except for irradiation time, and the results are revealed in Table 2. When butyrophenone in which the γ-position of a carbonyl group is primary was subjected to photoreaction, conversion was low and 3-benzoyl propionaldehyde or 3-benzoyl propionic acid, the expected oxidation product, could not be detected. The photoreaction of β-naphthyl pentyl ketone afforded the expected 1,4-dicarbonyl compound while, in the case of α-naphthyl pentyl ketone, conversion was low and the 1,4-dicarbonyl compound could not be detected.

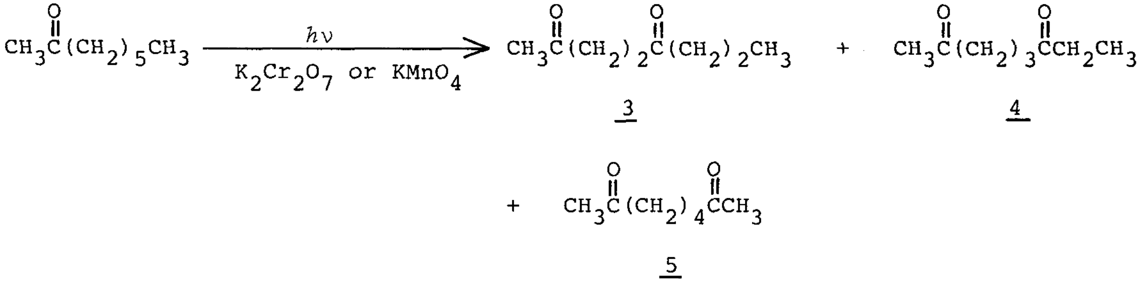
Table 2. Photoreaction of aryl ketones in the presence of $K_2Cr_2O_7$

Aryl ketone	Conversion[a]	Product[b]	Yield[a]
 $Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4CH_3$	95 %	 $Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2CH_3$	67 %
 $Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_3CH_3$	90 %	 $Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$	71 %
 $Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{CH_3}{\overset{\mid}{C}H}\text{-}(CH_2)_2CH_3$	95 %	 $Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{CH_3}{\overset{\mid}{C}H}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$	52 %
	100 %[c]		54 %[c]
	50 %		62 %
	70 %		57 %
	95 %		45 %

[a] Irradiation time=30 hr. Determined after isolation by a column-chromatography.

[b] Identified by NMR, IR, and MS spectra. [c] Irradiation time=16 hr.

Next, the photooxidation of alkyl ketone was also investigsted. 2-Octanone was irradiated in an aq.HCl-CH_3CN solution containing $K_2Cr_2O_7$ under a nitrogen atmosphere with a high- or low-pressure Hg lamp to afford a mixture of regioisomeric dicarbonyl compounds 3, 4, and 5 in only low yields. The photoreaction of 2-octanone in the presence of $KMnO_4$ instead of $K_2Cr_2O_7$ resulted also in formation of a mixture of 3, 4, and 5.



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}(CH_2)_5CH_3} \xrightarrow[\mathrm{K_2Cr_2O_7\ or\ KMnO_4}]{h\nu} \underset{\mathbf{3}}{\mathrm{CH_3\overset{\overset{O}{\|}}{C}(CH_2)_2\overset{\overset{O}{\|}}{C}(CH_2)_2CH_3}} + \underset{\mathbf{4}}{\mathrm{CH_3\overset{\overset{O}{\|}}{C}(CH_2)_3\overset{\overset{O}{\|}}{C}CH_2CH_3}} + \underset{\mathbf{5}}{\mathrm{CH_3\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}CH_3}}$$

Since the molar n,π^* absorption coefficient of 2-octanone is low relative to that of aromatic ketones, the photoreaction of oxidants might preferentially occur to generate some radical species which in turn abstract a hydrogen at random from alkyl chain of the ketone followed by oxidation with oxidants. Photoreaction of a solution containing 2-octanone and $K_2Cr_2O_7$ was performed in the presence of a sensitizer such as benzene or anisole with expectation to raise the fraction of light absorbed by 2-octanone. 2-Octanone, however, was only recovered and dicarbonyl compounds were not produced at all.

References and Note

1) P. J. Wagner and R. G. Zepp, J. Am. Chem. Soc., 94, 288 (1972); P. J. Wagner, P. A. Kelso, and R. G. Zepp, ibid., 94, 7480 (1972).
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