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THE PHOTOINDUCED REACTIONS OF BENZYL METHYL KETONE[1]

Y. OGATA, K. TAKAGI and Y. IZAWA

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

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Abstract—The photochemical reaction of benzyl methyl ketone (I) has been studied in n-hexane and t-butanol. The rearrangement products, *o*-methylacetophenone (II) and/or *p*-methylacetophenone (III), are obtained in poor yield, together with a reductive dimerization product, substituted pinacol (IV), and derivatives of benzyl radical, bibenzyl (V) and toluene (VI). The ratio of III to V tends to increase with lowering concentrations of reactants, but it is little affected by the irradiation time and reaction temperature.

SINCE the photochemical rearrangements of aromatic esters to hydroxyketones reported by Anderson *et al.*,[2] a number of photochemical rearrangements of aryl esters,[3] anilides,[4] aryl ethers,[5] aryl sulphonates[6] and sulphonamides[7] have been investigated, but there has been no report on the photochemical rearrangement of aromatic ketones. In our preliminary experiments on the photochemical reaction of benzyl methyl ketone (I) in n-hexane, a rearrangement product, *p*-methylacetophenone, was isolated together with other products. The present paper summarizes our results on the photochemistry of I and includes a novel rearrangement occuring in n-hexane and t-butanol.

RESULTS AND DISCUSSION

Irradiation of benzyl methyl ketone in n-hexane. Irradiation of benzyl methyl ketone (I) (λ_{max}^{EtOH} 2800 Å, log ε 2·24) in n-hexane in nitrogen atmosphere gave *p*-methylacetophenone (III, 0·4%), 1,2-dimethyl-1,2-dibenzylglycol (IV, 11·2%), bibenzyl (V, 8·5%) and an unknown polymer (0·6%). These photoproducts were identified by comparison with authentic samples, gas chromatography (GLC), mixed m.ps and/or IR spectrography. The formation of *p*-methylacetophenone in this reaction is of interest, since it constitutes a novel photochemical rearrangement.

If a molecule of benzyl methyl ketone is irradiated by 2800 Å light, its excitation energy should be about 102 kcal/mole. Since the acetyl-benzyl bond strength is ca. 63 kcal/mole,[8] this value is sufficient for the formation of benzyl and acetyl radicals. A lower concentration of I results in a higher ratio of the rearrangement product *vs* the radical-coupling product, bibenzyl (V). This may be explained by the lower efficiency of secondary recombination of two benzyl radicals to give V at the lower concentration of I (Table 1).

Table 1 compares the use of a high pressure mercury lamp (immersion lamp) with a low pressure mercury lamp. The former lamp emits the light of wavelength longer than 2800 Å, while the latter emits almost exclusively 2537 Å. These lamps show no appreciable effect on the ratio of III to V. Therefore, the excitation of I by the benzenoid absorption, i.e., λ_{max}: 2532, 2590 and 2650 Å with log ε: 2·39, 2·44

TABLE 1. THE EFFECT OF THE CONCENTRATION OF BENZYL METHYL KETONE I ON THE MOLAR RATIO OF *p*-METHYLACETOPHENONE III VS. BIBENZYL V IN THE IRRADIATION OF I IN n-HEXANE UNDER NITROGEN ATMOSPHERE AT ROOM TEMPERATURE FOR 4 HR

High press Hg lamp		Low press Hg lamp	
[I] ($\times 10^2$ M)	[III]/[V] ($\times 10^2$)	[I] ($\times 10^2$ M)	[III]/[V] ($\times 10^2$)
2·42	0·64	2·37	1·07
1·24	1·72		
4·50	5·32	4·66	4·9

and 2·40, respectively, as well as by the n-π^* absorption of carbonyl group at 2800 Å, may cause the cleavage of I to benzyl and acetyl radicals.

The irradiation of a n-hexane solution of 0·012 M I was carried out at −55° and 25° for 4·5 hr. The benzyl radical is more stable at the lower temperature and this favours the formation of V; hence the ratio of III to V at −55° (0·0109) is smaller than at 25° (0·0172), where the yield of III is almost constant at different temperatures. This phenomenon suggests that the rearrangement to III may be intramolecular and not intermolecular.

With an increase of irradiation time, the amount of rearranged product III is not increased but the ratio VI to V is increased, which implies that the cleavage of I to benzyl and acetyl radicals is almost completed during the early stages of irradiation of dilute solutions of I. In fact, I (0·002 M) was almost completely decomposed after irradiation for ca. 1 hr. The increase in the ratio VI to V may be explained by the secondary photodecomposition of bibenzyl (V) forming toluene (VI) as shown in Table 2.

TABLE 2. THE EFFECT OF THE IRRADIATION TIME ON THE MOLAR RATIO OF TOLUENE VI VS. BIBENZYL V IN THE IRRADIATION BY A HIGH PRESSURE MERCURY LAMP IN A 0·002 M I n-HEXANE SOLUTION AT ROOM TEMPERATURE

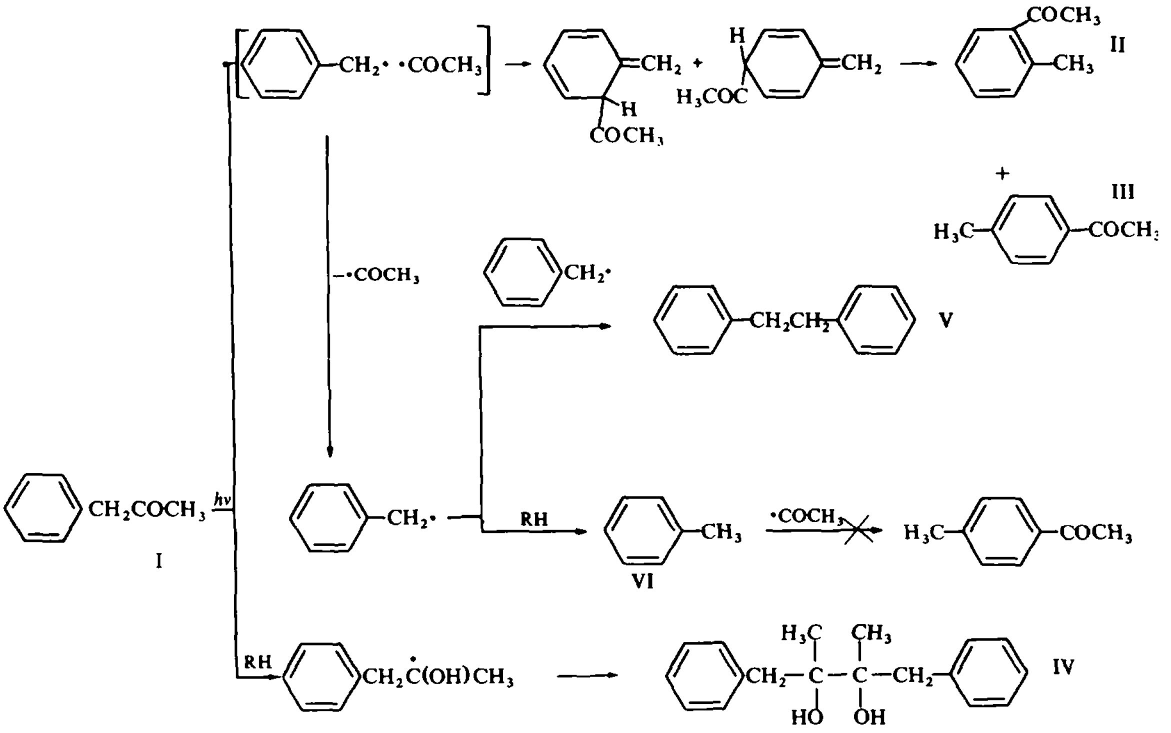
Irrad. time (hr)	1	4	8
[VI]/[V]	1·2	7·0	13·1
Yield of V (%)	23·0	8·5	6·8

As pinacol formation via the n-π^* excitation of I occurs readily in n-hexane having secondary hydrogen atoms, t-butanol was used instead.

The irradiation of I in t-butanol gave *o*-methylacetophenone (II; 0·9%), a rearrangement product which could not be observed in n-hexane. In addition to II, compound III (0·3%) was obtained together with V (11·3%) and VI (6·1%).

In contrast, no rearrangement product was observed in either ethanol or benzene but a certain amount of acetophenone was identified in the reaction in benzene. The formation of acetophenone indicates the presence of acetyl radical.

Probable reaction pathways to account for the observed products are outlined in the following scheme:



The methylacetophenone may be formed either by an intramolecular rearrangement via a quinonoid transition state or by an intermolecular reaction of toluene with acetyl radicals; the latter pathway is conceivable, since acetophenone is formed during irradiation of I in benzene and the yield of methylacetophenones should increase by adding toluene if the intermolecular mechanism operates. But as the yield was not affected by the addition of toluene, the intramolecular mechanism via a quinonoid state takes place.

As only *p*-methylacetophenone was identified as rearrangement product in n-hexane, both the *o*- (0·9 %) and *p*-isomers (0·3 %) were observed in t-butanol. The total yield of rearrangement product was slightly higher in t-butanol than in n-hexane. A similar result was observed in the photochemical Fries rearrangement of *p*-tolyl benzoate, i.e., the total yields of rearrangement products in cyclohexane and in isopropanol were 25 % and 34 %, respectively.[3d]

Formation of the *o*-isomer in t-butanol but not in n-hexane may be due both to the solvent effect on the rate of rearrangement[8] and the solvation of I, i.e., solvation of the carbonyl group of I takes place in t-butanol but not in n-hexane and therefore, the resulting solvated acetyl radical migrates to the *ortho* position of the aromatic ring which is closer to the benzyl carbon atom than the *para* position.

These results are consistent with those observed in other photochemical rearrangements.[3d,9] Thus the rate of the photochemical Wallach rearrangement of α-2-phenylazoxynaphthalene to 1-hydroxy derivatives is faster in alcohol than in aliphatic hydrocarbons, i.e., very slow in light petroleum, slow in benzene and relatively fast in ethanol.[9] Similarly, the ratios of *o*-isomer to *p*-isomer in the photochemical Fries rearrangement of phenyl benzoate in cyclohexane and in dioxan have been reported to be 0·38 and 0·57, respectively.[3d]

Finally, it was confirmed that the *o*- and *p*-methylacetophenones cannot be reduced to the corresponding pinacols on irradiation. This fact agrees with the result by Beckett *et al.*[10]

EXPERIMENTAL

UV spectra were measured by a Shimadzu Type SV-50A automatic spectrophotometer, and IR spectra by a Perkin–Elmer Type 337 grating IR spectrophotometer. The GLC was carried out by a Yanagimoto GCG-220 gas chromatograph.

The irradiation was carried out using an immersion type Halos 300 W high press Hg vapour lamp, whose total relative energy of radiation below 3000 Å was ca. 90 % to that of 3650–3663 Å, and an immersion type Halos low press Hg vapour lamp rich in 2537 Å radiation.

n-Hexane was passed through silica gel and then distilled, b.p. 65–68°.

Benzyl methyl ketone. α-Phenylacetoacetonitrile, m.p. 82°, was prepared by the reaction of benzyl cyanide, b.p. 115–123°/26 mm, with dry EtOAc[11] and was converted to benzyl methyl ketone by the addition of conc H_2SO_4 and then water at −10° followed by heating this soln on a water bath for 2 hr to complete the reaction, b.p. 108–109·5°/26 mm (lit[12]. 109–112°/24 mm), n_D^{20} 1·5169 (lit.[13] 1·5168), m.p. of its semicarbazone 193–195° (lit.[14] 194–195°), λ_{max}^{EtOH} (log ε) 2485 (2·29), 2530 (2·39), 2590 (2·44), 2650 (2·40) and 2800 (2·24) Å.

o-*Methylacetophenone.* This was prepared by the chromic acid oxidation[15] of α-(*o*-tolyl)ethanol, which was synthesized by the reaction of the Grignard reagent of *o*-bromotoluene and acetaldehyde, b.p. 122–125°/47 mm (lit.[15] 105°/20 mm), λ_{max}^{EtOH} (log ε) 2430 (3·69), 2840 (2·72) and 3280s (1·48) Å.

p-*Methylacetophenone.* This was prepared by the Friedel-Crafts acetylation of toluene, b.p. 114–115°/27 mm (lit.[16] 225/736 mm), n_D^{20} 1·5342 (lit.[16] 1·5335), λ_{max}^{EtOH} (log ε) 2510 (3·14) Å.

Bibenzyl. This was prepared by Friedel-Crafts reaction of dichloroethane with benzene.[17] m.p. 51·3–51·8° (lit.[17] 51–52°).

Typical irradiation of benzyl methyl ketone (I) *in a n-hexane.* A 0·0038 M soln (600 ml) of I (0·31 g) was irradiated at 24° under N_2 with a high press Hg vapour lamp for 4 hr. After irradiation, the ppt was filtered off and extracted with MeOH and then the solvent was evaporated, giving pinacol I (11·2 %). The product was purified by sublimation, m.p. 101·0–101·5° (lit.[18] 101–102°), ν_{max} 3400 cm^{-1} (OH). The MeOH-insoluble (0·6 %) polymerized material did not melt below 300°.

The filtrate was carefully condensed under reduced press. The analysis of the condensed soln was carried out by means of GLC employing a Yanagimoto Model GCG-220 operated with both 3·0 m × 4 mm and 2·25 m × 4 mm columns, the former was packed with Silicone DC 550 (30 wt %) on Celite 545 of 80–100 mesh and the latter with polyethylene succinate (20 wt %) on Celite 545 of 80–100 mesh, using H_2 as carrier gas (50 and 28 ml/min, respectively) at 190°.

The agreement of the retention times of the peaks with those of authentic samples, i.e., *p*-methylacetophenone, bibenzyl and toluene, established their identity. Estimation of these products was by means of GLC using diphenylmethane as an internal standard and the yields of *p*-methylacetophenone (0·4 %), bibenzyl (8·5 %) and toluene (12·9 %) were calculated on the basis of benzyl methyl ketone used.

Bibenzyl was isolated by preparative gas chromatography and identified by ν_{max} and m.m.ps 51–52° (lit.[17] 51–52°) with an authentic sample.

Typical irradiation of I *in t-butanol.* A soln (400 ml) of 0·0082 M I (0·44 g) was irradiated similarly at 28° for 10 hr. After irradiation, the mixture was carefully condensed under reduced press, and analysed by GLC. Under conditions similar to those used in n-hexane, *o*-methylacetophenone (0·9 %), *p*-methylacetophenone (0·3 %), toluene (6·1 %) and bibenzyl (11·3 %) were identified.

Typical irradiation of I *in benzene.* A soln (300 ml) of 0·0126 M I (0·50 g) was irradiated as described at 25° for 4 hr. After condensation of the reaction mixture by evaporation, acetophenone was identified by means of GLC using an authentic sample.

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