Elimination Reactions Induced by Photoenolization of *o*-Alkylbenzophenones

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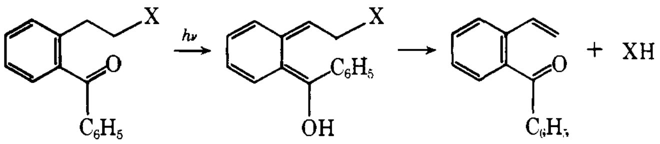
Abstract: 2-Substituted *o*-ethylbenzophenones undergo efficient elimination of the 2-substituent on irradiation. No deuterium is incorporated upon irradiation in methanol-d_1. Nevertheless inefficiencies in the reactions are thought to be due in part to reketonization of intermediate photo-enols. The absence of exchange is attributed to the formation of stereoisomeric photo-enols. One of these probably undergoes quantitative elimination and the other reketonizes or eliminates at rates that are faster than the rate of exchange. The latter isomer can be intercepted by base as shown by base acceleration of both photo-exchange in *o*-ethylbenzophenone and photo-elimination from the 2-substituted derivatives. The possibility that these reactions proceed through an excited state of the photo-enols is less likely but has not unambiguously been eliminated.

It has previously been shown that *o*-alkylbenzophenones undergo light-induced enolization. The resulting *o*-quinoid species have been shown to reketonize,[2] react with dienophiles,[2,3] and undergo both dark and photocyclizations.[4,5] During an investigation of potential photochemically removable protecting groups, it occurred to us that the powerful driving force of rearomatization of the *o*-quinoid intermediate might be used to effect elimination of substituents that would be relatively unreactive in the benzophenone precursor **1**.



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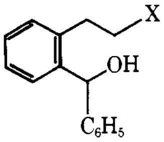

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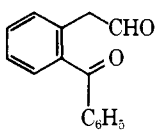

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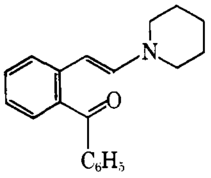

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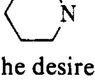
a, X = HO
b, X = $(C_6H_5)_3CO$
c, X = *p*-$CH_3C_6H_4SO_3$
d, X = *p*-$C_2H_5OCOC_6H_4NHCO_2$
e, X = *p*-$O_2NC_6H_4CO_2$
f, X =



For the synthesis of the desired compounds **1**, 1-phenylindene was ozonized in ether–methanol followed by sodium borohydride reduction to give *o*-(2-hydroxyethyl)benzhydrol (**2a**) (80%). Treatment of **2a** with trityl chloride in pyridine gave the ether **2b** (97%). Oxidation of **2a** and **2b** with activated manganese dioxide yielded the benzophenones **1a** and **1b**, respectively, in near quantitative yields. In addition, **1a** was esterified with tosyl chloride, *p*-nitrobenzoyl chloride, and *p*-carbethoxyphenyl isocyanate in pyridine to give the respective esters **1c** (70%), **1e** (84%), and **1d** (60%). Preparation of **1f** was carried out by dimethyl sulfide treatment of the 1-phenylindene ozonolysis mixture to give **3**, conversion to **4** with piperidine and *p*-toluenesulfonic acid in benzene, and reduction with formic acid in benzene (overall yield 16%).

The photochemical behavior of degassed solutions of **1** in methanol or acetonitrile was similar with either 2537-Å light or Pyrex-filtered light from a high-pressure mercury source. Elimination of the substituent from **1c–f** was observed with formation of the corresponding acid or amine in yields of 88–95% (Table I). The yields of *o*-vinylbenzophenone (**5**) were somewhat lower (>75%) due to a secondary photochemical reaction which has not been investigated. The trityl derivative **1b** gave a 62% yield of triphenylcarbinol but the quantum efficiency was much lower, and thus only a trace of unchanged *o*-vinylbenzophenone could be recovered. The primary alcohol **1a** likewise underwent only slow reaction and only a complex mixture of products was obtained.

A number of experiments were conducted to elucidate the mechanism of the photo-elimination reaction. Evidence that the ketone group was required was obtained from the observation that the benzhydrol derivative **2e** failed to undergo any photochemical reaction under conditions where **1e** was completely destroyed. Although this was consistent with the hypothesis that the reaction proceeds through the enol, attempts to trap the enol by irradiation of **1e** with dimethyl acetylenedicarboxylate proved unsuccessful. Moreover upon photolysis of **1e** in CH_3OD with up to 60% conversion to products, less than 0.5% incorporation of deuterium in either the starting material or the *o*-vinylbenzophenone product was obtained. By contrast, under similar conditions, *o*-methylbenzophenone readily forms an adduct with dienophiles and undergoes photo-induced deuterium exchange.[2,3,8] Thus either the species analogous to the trappable *o*-methylbenzophenone photo-enol was not formed from **1e** or, if it was formed, it underwent elimination too rapidly to permit trapping.

Direct evidence that an enol was in fact formed was obtained by irradiation (Vycor filter) of a degassed solution of **1e** in 3:5 ether–ethanol at 150 K. Under these conditions, both **1e** and *o*-methylbenzophenone formed yellow transients (λ_{max} near 400 nm). Both species were bleached by irradiation with >430 nm light, a process which had previously been shown to be due to cyclization to a hydroxydihydroanthracene (**6**).[4] Moreover upon then exposing the solutions to air and adding sodium hydroxide both solutions displayed the bright yellow color of the corresponding hydroxyanthracene anion (**7**, R = H or $CH_2OCOC_6H_4NO_2$).

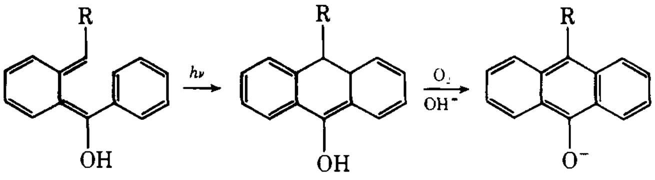


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Table I. Photo-Elimination Yields and Quantum Yields (ϕ) of 2-Substituted *o*-Ethylbenzophenones (1)

	Yield, %[a]			ϕ[b]	
Reactant	XH	5	ϕ[b]	$3.7 \times 10^{-3} M$ Na_2CO_3	$4 \times 10^{-3} M$ CH_3COOH
1c	95	90	0.47	0.52	0.40
1d	91	84	0.22	0.28	0.24
1e	93	75	0.16	0.24	0.16
1f	80	77	0.25	0.16	0.48
1 (X = H)			0.15[c]	0.28[c]	0.14[c,d]

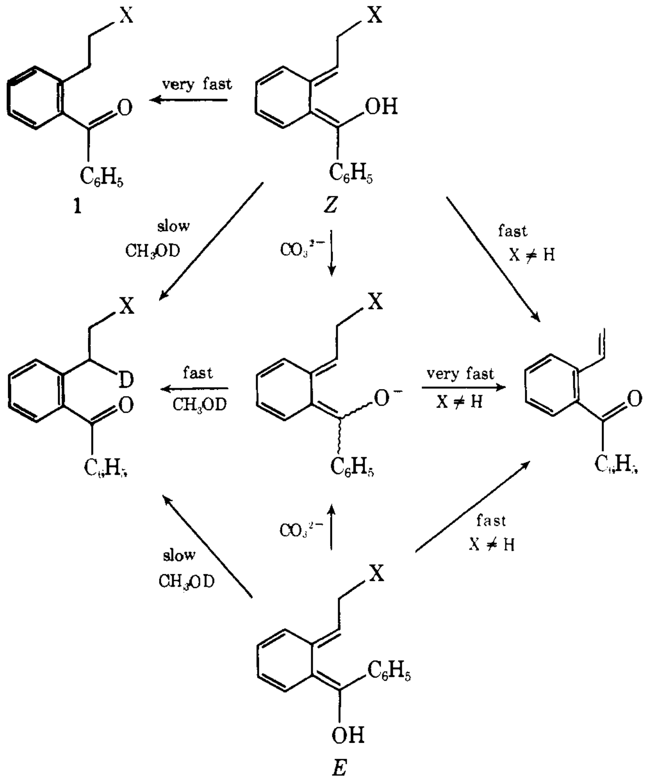
[a] Irradiation of acetonitrile solutions with Pyrex-filtered light. [b] Irradiations carried out in methanol with 2537-Å light. [c] Quantum yields for deuterium exchange. [d] $5.6 \times 10^{-4} M$ CH_3COOH.

The thermal disappearance of the 400-nm absorption formed by irradiation of **1e** at 150 K was first order and about 30% faster than the rate of disappearance of the corresponding species formed from *o*-methylbenzophenone. On irradiation of a methanol solution of *o*-ethylbenzophenone,[9] which would be expected to be structurally closer to **1** than the *o*-methyl derivative, a yellow transient was produced which required several minutes to fade even at room temperature. By contrast no color was observable on irradiation of **1e** at this temperature.

These data appear to provide compelling evidence that **1** (X ≠ H) was converted to an enol which had a greatly reduced lifetime relative to that of **1** (X = H), presumably because of rapid elimination of the X substituents. The photoenolization and photo-elimination reaction paths should therefore be expected to proceed through analogous intermediates up to and including the photo-enol. Evidence that one of these was the triplet state of **1** was obtained from the effect of naphthalene on the photo-elimination reaction of **1c**. Quenching was observed and a linear Stern–Volmer plot could be constructed from which the lifetime of the quenched excited state was estimated to be 1.0×10^{-6} sec (assuming a diffusion rate constant in methanol of 1.1×10^9 M^{-1} sec^{-1}).[10] Interestingly this is substantially longer than the lifetime of a species identified by Porter and Tchir as the triplet of 2,4-dimethylbenzophenone (2.8×10^{-8} sec in ethanol), but it is very similar to another transient (1.7×10^{-6} sec) to which they make no definite assignment.[11] The possibilities must therefore be entertained either that the 2.8×10^{-8} sec intermediate is not the triplet ketone or that two ketone triplet states are observable by their flash photolysis experiments.[12]

Despite the implication of a short-lived enol intermediate in the elimination reaction, there remains the possibility that rapid elimination of XH occurs from an intermediate other than the enol. Elimination might occur directly from either the ketone or enol triplets, both of which have been suggested as intermediates.[11a,13] Such an interpretation is permitted by the data but is not required. Moreover it does not obviate the need to assume elimination from ground-state enol to explain the short lifetime of this species. It is interesting to note that the quantum yields of elimination (Table I) were related to the *ground* state leaving abilities of the X substituents. Tosyl and piperidinium were most efficient, and *p*-nitrobenzoate was least efficient. The reaction was accelerated by base as shown by the effect of sodium carbonate on the quantum yields of **1c–e** and by the remarkably efficient loss of even an unprotonated piperidinyl group under basic conditions.

The above interpretation of the reaction, in which an enol is formed which undergoes rapid elimination, does not explain the variations observed in the quantum yields with base and with different leaving groups. If elimination from the enol were sufficiently rapid to preclude reketonization, acceleration of this step with base could not increase the quantum efficiency of the reaction. An additional reactive intermediate is therefore required. It has previously been shown that flash photolysis of 2,4-dimethylbenzophenone gives stereoisomeric ground-state enols, a short-lived *Z* isomer and a long-lived *E* isomer.[11] The *E* isomer presumably must reketonize by delivery of a proton from the solvent. This reaction may be slow relative to elimination, and thus elimination competes efficiently with reketonization and trapping reactions. On the other hand, the *Z* isomer can ketonize very rapidly through an allowed sigmatropic process without incorporation of a solvent proton. This process may be sufficiently rapid that deuterium exchange or trapping would normally not be observable. The higher quantum yields observed with the more active leaving groups may be explained by assuming that elimination from the *Z* isomer partially competes with reketonization and that both processes are more rapid than deuterium exchange. Increased quantum yields with base can similarly be explained by catalyzed elimination from *Z*.



This scheme also serves to predict, at least qualitatively, the effect of base on the rate of deuterium exchange of *o*-ethylbenzophenone (**1**; X = H) in methanol-d_1 (Table I). The quantum yield of exchange with 2537-Å light at room temperature was found to increase from 0.15 to 0.28 upon inclusion of 3.7×10^{-3} M sodium carbonate. The long-lived *E* photo-enol presumably must incorporate a solvent proton (deuteron) during ketonization whether or not base is present. The increase in the quantum efficiency of exchange with added base thus suggests that deuterium incorporation occurs during ketonization of the *Z* isomer when this process is base catalyzed. With base an enolate anion can be formed from the *Z* isomer which can reketonize with incorporation of a solvent deuterium or undergo rapid elimination when X is present as a suitable leaving group. Evidence that the eliminatin process is faster than deuteration was obtained from the observation that irradiation of **1e** in methanol-d_1 in the presence of sodium carbonate failed to lead to incorporation of deuterium in either the starting material or products.

Table II. Effect of Sodium Carbonate on the Quantum Yield of Deuterium Exchange of 0.1 *M* *o*-Ethylbenzophenone in Methanol-d_1[a]

$[Na_2CO_3] \times 10^4, M$	ϕ	$[Na_2CO_3] \times 10^4, M$	ϕ
0	0.153	4.72	0.273
0.71	0.182	6.45	0.280
1.26	0.197	7.4	0.285
1.89	0.204	8.33	0.285
2.83	0.240	37.8	0.277
3.74	0.268		

[a] Reactions monitored by NMR.

It remains unexplained why the quantum yield for base-catalyzed exchange in **1** (X = H) is less than for base-catalyzed elimination from **1c** (cf. Table I). If the above interpretations are correct, every photo-enolization step should lead to exchange in **1** (X = H) if sufficient base is present. The quantum yield for elimination from **1c** should therefore not exceed the exchange quantum yield, except in the very unlikely event that the presence of the leaving group X somehow increases the quantum yield of the primary photo-enolization process.

The effect of the base concentration on the quantum yield for exchange of **1** (X = H) was therefore studied (Table II). If the *E* isomer always incorporates a solvent proton upon reketonization and the *Z* isomer exchanges only by base catalysis, it can be shown that

$$\frac{1}{\phi - \phi_E} = \frac{1}{\phi_Z} + \frac{1}{\phi_Z}\frac{k_d}{k_b[B]}$$

where ϕ_Z is the quantum yield of formation of the *Z* enol, k_d is the unimolecular rate constant for its reketonization, and k_b is the rate constant for exchange of the *Z* enol catalyzed by base (B). The quantum yield in the absence of base is assumed to be equal to that for the formation of the *E* enol (ϕ_E).

Unfortunately a plot of $1/(\phi - \phi_E)$ against $1/[B]$ (Figure 1) deviates significantly from linearity at high base concentrations possibly because of excited state quenching by the base. At lower concentrations, despite much scatter, the data permit construction of a linear plot. From the intercept, the total quantum yield for photo-enolization ($\phi_E + \phi_Z$) is estimated to be ≤ 0.45, not much less than the maximum quantum yield observed for **1c**. Thus with sufficient base, the quantum yields for both reactions may approach a limiting value for the photo-enolization reaction as expected by the above mechanism. The fact that the quantum yields for exchange of **1** (X = H) are less than for elimination from **1c** both with or without base suggests that some uncatalyzed elimination occurs from the *Z* enols when sufficiently good leaving groups are present.

Experimental Section

Preparative Photolyses. Acetonitrile solutions (150 ml) of the ketones (150 mg) were deoxygenated by bubbling with nitrogen and irradiated in Pyrex flasks with light from a GE BH6 high-pressure Hg lamp. Irradiations were continued (3-7 hr) until the starting material could no longer be detected by TLC. The elimination products were compared with authentic materials. *o*-Vinylbenzophenone[14] was purified by preparative TLC (silica gel, 4:1 hexane-ethyl acetate): λ_{max} (CCl_4) 1660 cm^{-1}; λ_{max} (CH_3OH) 244 nm (ϵ 24000), 270 (7500), 290 (2600), and 330 (430); NMR ($CDCl_3$) δ 5.25 (q, 1 H, J_{AX} = 11 Hz, $J_{AB} \sim$ 1 Hz), 5.73 (q, 1 H, J_{BX} = 17 Hz, J_{AB} = 1 Hz), 6.85 (q, 1 H, J_{AX} = 11 Hz, J_{BX} = 17 Hz), 7.6 ppm (m, 9 H); mass spectrum *m/e* 208 (M^+).

Anal. Calcd for $C_{15}H_{12}O$: C, 86.49; H, 5.77. Found: C, 86.23; H, 6.06.

Low Temperature Photolyses. Solutions of the ketones in 3:5 ether-ethanol mixtures were degassed in quartz cuvettes by freezing and thawing. The cells were cooled to 150 K in an Air Products Cryo-tip equipped with quartz windows. A 450-W medium-pressure mercury lamp fitted with a Vycor filter was used to irradiate the solutions for about 45 sec. The disappearance of the thus-formed transients was monitored at 400 nm on a Cary 15 spectrophotometer. Linear first-order decay was observed: *o*-methylbenzophenone, 1.5×10^{-3} sec^{-1}; **1e**, 2.0×10^{-3} sec^{-1}.

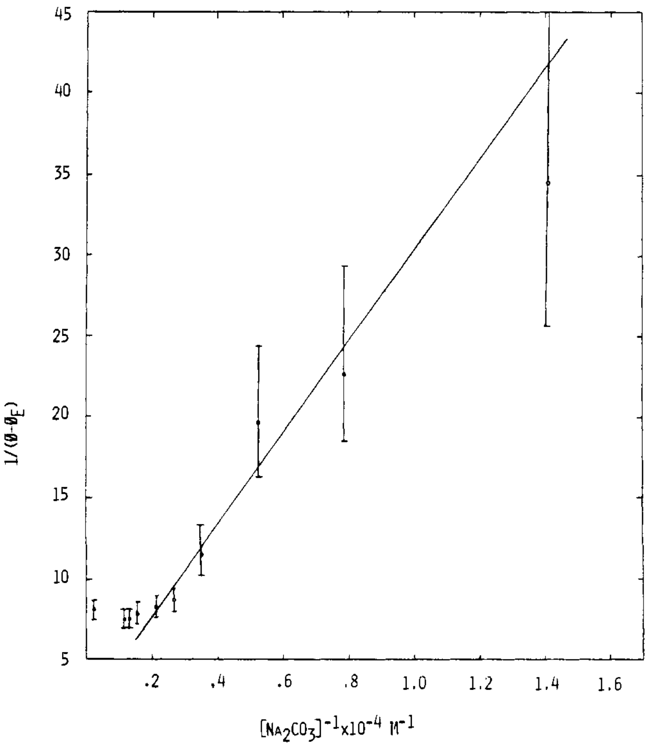


Figure 1. Effect of sodium carbonate on the quantum yield of exchange of 0.1 *M* *o*-ethylbenzophenone in methanol-d_1. Error bars are based on an assumed average error of ±0.01.

Quantum Yields. Methanol solutions were degassed in a sealed Y-shaped cell and irradiated with 2537-Å light from a 140-W medium-pressure Hg arc employing a $NiSO_4$-$CoSO_4$-I_2-KI filter.[15] The light intensity was determined by potassium ferrioxalate actinometry. The appearance of *o*-vinylbenzophenone was monitored near 240 nm and was initially linear with time. Quantum yields were calculated taking into account unabsorbed light and light absorbed by naphthalene in the quenching experiments. Deuterium exchange quantum yields were determined using a Rayonet photochemical reactor equipped with 2537-Å lamps. Sealed quartz tubes containing the ketone in 3 ml of methanol-d_1 were irradiated in a merry-go-round apparatus inside a quartz jacket containing a $NiSO_4$-$CoSO_4$ filter solution. Deuterium incorporation was monitored both by NMR (0.1 *M* ketone) and mass spectroscopy (1.1×10^{-3} *M* ketone).

***o*-(2-Hydroxyethyl)benzhydrol (2a).** A solution of 1-phenylindene[16] (5.0 g, 0.026 mol) in 250 ml of 1:4 ether-methanol was treated with ozone at −80°. Upon completion of ozonolysis (40 min), a solution of 5 g of sodium borohydride in 180 ml of 50% ethanol was added dropwise at 0° with stirring. After stirring at room temperature for 15 hr, the solution was evaporated in vacuo and the residue extracted with ether. Evaporation of the extracts yielded the crude diol **2a** (4.75 g, 82%) which was recrystallized from 1:1 hexane-ethyl acetate, mp 96-99° (reported[17] 97°).

Anal. Calcd for $C_{15}H_{16}O_2$: C, 79.00; H, 7.02. Found: C, 78.85; H, 7.08.

***o*-(2-Hydroxyethyl)benzophenone (1a).** To a solution of *o*-(2-hydroxyethyl)benzhydrol (**2a**) (0.3 g, 1.32 mmol) in ether (30 ml) was added 3 g of freshly prepared active manganese dioxide. The mixture was stirred at room temperature for 4 hr. After removal of the inorganic materials, the organic filtrate was evaporated to give an oily product (0.29 g, 95%) which was purified for analysis by TLC on silica gel (2:1 hexane-ethyl acetate): λ_{max} (CCl_4) 3440 and 1665 cm^{-1}; λ_{max} (CH_3CN) 249 nm (ϵ 11500), 280 (2380), 290 (1440), and 330 (77); NMR ($CDCl_3$) δ 2.9 (t, 2 H, *J* = 6 Hz), 3.05 (s, 1 H), 3.8 (t, 2 H, *J* = 6 Hz), and 7.1–8.0 ppm (m, 9 H); mass spectrum *m/e* 226 (M^+), 209 ($M^+ - OH$).

Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.65; H, 6.19. Found: C, 79.11; H, 6.28.

***o*-(2-Hydroxyethyl)benzophenone *p*-Toluenesulfonate (1c).** To a solution of *o*-(2-hydroxyethyl)benzophenone (160 mg, 0.7 mmol) in dry pyridine (6 ml) was added *p*-toluenesulfonyl chloride (150 mg, 0.8 mmol) in portions with magnetic stirring at 0° under nitrogen. After the addition was complete (10 min), the mixture was stirred at 0–5° for 16 hr, added to 5% aqueous sodium bicarbonate, and extracted with ethyl acetate. Evaporation of the solvent gave a light yellow oil which, after purification by preparative TLC on silica gel (2:1 hexane–ethyl acetate), weighed 120 mg. The oily product was unstable and decomposed slowly over a period of days even when stored in the cold: λ_{max} (CCl_4) 1660 cm^{-1}; λ_{max} (CH_3OH) 250 nm (ϵ 14000), 272 (4760), 280 (3030), and 320 (183); NMR ($CDCl_3$) δ 2.4 (5.3 H), 3.1 (t, 2 H, *J* = 7 Hz), 4.3 (t, 2 H, *J* = 7 Hz), and 7.2–7.8 ppm.

***o*-(2-Hydroxyethyl)benzophenone *p*-Nitrobenzoate (1e).** To a solution of *o*-(2-hydroxyethyl)benzophenone (0.57 g, 2.52 mmol) in dry pyridine (10 ml) was added 0.7 g of *p*-nitrobenzoyl chloride in portions at 0° stirring under nitrogen. After the addition, the mixture was stirred at room temperature for 20 hr and then poured into 100 g of ice–water with vigorous stirring. The white solid precipitate was dried (0.94 g), dissolved in chloroform (100 ml), and washed with 5% sodium bicarbonate. Evaporation of the chloroform solution yielded 0.79 g (84%) of crude product which, after recrystallization from ether–petroleum ether, melted at 88–89°: λ_{max} ($CHCl_3$) 1725, 1660 cm^{-1}; λ_{max} (CH_3OH) 252 nm (ϵ 27800), 280 (9700), 290 (5350), and 340 (458); NMR ($CDCl_3$) δ 3.2 (t, 2 H, *J* = 7 Hz), 4.6 (t, 2 H, *J* = 7 Hz), and 7.2–8.4 ppm (m, 13 H).

Anal. Calcd for $C_{22}H_{17}O_5N$: C, 70.40; H, 4.53; N, 3.73. Found: C, 70.66; H, 4.75; N, 3.74.

***o*-(2-Hydroxyethyl)benzophenone *p*-(Ethoxycarbonyl)carbanilate (1d).** To a solution of *o*-(2-hydroxyethyl)benzophenone (0.12 g, 0.53 mmol) in dry benzene (4 ml) was added 0.1 g (0.54 mmol) of *p*-(ethoxycarbonyl)phenyl isocyanate. The mixture was stirred at room temperature for 30 min and then at 60° for 5 hr. Evaporation of benzene solution yielded the crude product which was purified by preparative TLC on silica gel (2:1 hexane–ethyl acetate) to give 0.14 g (60%): mp 111–112°; λ_{max} (KBr) 3320, 1740, 1660 cm^{-1}; λ_{max} (CH_3OH) 260 nm (ϵ 32600), 276 (26000), and 330 (222); NMR ($CDCl_3$) δ 1.39 (t, 3 H, *J* = 7.2 Hz), 3.10 (t, 2 H, *J* = 6.6 Hz), 4.36 (t, 2 H, *J* = 6.6 Hz), 4.39 (q, 2 H, *J* = 7.2 Hz), 7.05 (s, 1 H), and 7.3–8.1 ppm (m, 13 H).

Anal. Calcd for $C_{25}H_{23}O_5N$: C, 71.94; H, 5.40; N, 3.28. Found: C, 71.84; H, 5.60; N, 3.23.

***o*-[2-(Trityloxy)ethyl]benzophenone (1b).** To a solution of *o*-(2-hydroxyethyl)benzhydrol (0.1 g, 0.44 mmol) in dry pyridine (10 ml) was added 0.12 g (0.45 mmol) of trityl chloride in portions with stirring under nitrogen. The mixture was stirred at room temperature for 16 hr and then poured into 100 ml of ice–water with vigorous stirring. Extraction with ether and evaporation of the extracts afforded the crude *o*-[2-(trityloxy)ethyl]benzhydrol (0.21 g) which was purified by preparative TLC on silica gel (2:1 hexane–ethyl acetate) to give 0.16 g (78%); NMR ($CDCl_3$) δ 2.42 (s, 1 H), 3.2 (m, 4 H), 6.10 (s, 1 H), and 7.1–7.6 ppm (broad m, 24 H).

A solution of *o*-[2-(trityloxyl)ethyl]benzhydrol (0.11 g, 0.234 mmol) in ether (20 ml) was stirred with active manganese dioxide (1.4 g) for 2 hr at room temperature. Filtration and evaporation of the solvent in vacuo gave nearly pure **1b** (1.05 g, 97%) which on recrystallization from ether–petroleum ether melted at 147–149°: λ_{max} (KBr) 1660 cm^{-1}; λ_{max} (CH_3OH) 250 nm (ϵ 13700), 280 (3220), and 325 (119); NMR ($CDCl_3$) δ 3.20 (m, 4 H), 7.2–7.9 ppm (m, 24 H).

Anal. Calcd $C_{34}H_{28}O_2$: C, 87.20; H, 5.98. Found: C, 86.94; H, 6.17.

***o*-(2-Piperidinoethyl)benzophenone (1f).** A solution of 1-phenylindene (4.0 g, 0.0208 mol) in 1:4 ether–methanol at −80° (250 ml) was treated with ozone. After the ozonolysis was complete, 15.0 g (0.24 mol) of dimethyl sulfide was added, and the mixture was stirred at room temperature overnight. The solvents were evaporated in vacuo, and an ether solution of the residue was washed with water and evaporated to a yellow oil (4.7 g). Vacuum distillation gave α-(2-benzoylphenylacetaldehyde) (3.7 g, 80%): bp 159–161° (0.8 mm); NMR ($CDCl_3$) δ 3.9 (d, 2 H, *J* = 2 Hz), 7.1–7.8 (m, 9 H), and 9.8 ppm (t, 1 H, *J* = 2 Hz). To a solution of this aldehyde (2.73 g, 0.012 mol) in benzene (70 ml) were added 1.74 g (0.02 mol) of piperidine and 10 mg of *p*-toluenesulfonic acid. The mixture was heated at reflux for 4 hr under nitrogen. A Dean-Stark trap was used to remove the water. The solution was then treated with 1.4 g of 98% formic acid (0.03 mol) and stirred for an additional 2 hr at 60°. The residue obtained by evaporation of the solvent was taken up in 5% hydrochloric acid (100 ml) and washed with ethyl acetate. Neutralization of the aqueous solution with 5% NaOH solution, extraction with ether, and evaporation of the solvent gave the crude product (0.71 g, 20%). The product failed to crystallize even after chromatography (aluminum oxide, ether): λ_{max} ($CHCl_3$) 1665 cm^{-1}; λ_{max} (CH_3OH) 250 nm (ϵ 15000), 280 (3520), 290 (2180), and 330 (180); NMR ($CDCl_3$) δ 1.5 (s, 6 H), 2.4 (d, 4 H), 2.75 (m, 4 H), and 7.3–8.0 ppm (m, 9 H); mass spectrum *m/e* 293 (M^+).

Anal. Calcd for $C_{20}H_{23}NO$: C, 82.00; H, 7.85; N, 4.78. Found: C, 81.97; H, 7.90; N, 4.61.

***o*-(α-Hydroxybenzyl)phenethyl *p*-Nitrobenzoate (2e).** To a solution of *o*-(2-hydroxyethyl)benzhydrol (**2a**) (0.5 g, 0.22 mmol) in 10 ml of dry pyridine was added 0.6 g of *p*-nitrobenzoyl chloride at 0°. The mixture was stirred at room temperature for 30 hr and then poured into 100 ml of ice–water with vigorous stirring. The resulting suspension was acidified with 10% hydrochloric acid and extracted with ethyl acetate. The extracts were purified by preparative TLC (silica gel, 4:1 hexane–ethyl acetate) to give 0.7 g (85%) of the oily product: λ_{max} (CCl_4) 3500, 1725 cm^{-1}; NMR ($CDCl_3$) δ 2.5 (s, 1 H), 3.2 (t, 2 H, *J* = 7 Hz), 4.5 (t, 2 H, *J* = 7 Hz), 6.2 (s, 1 H), 7.4 (m, 9 H), and 8.2 ppm (m, 4 H); mass spectrum *m/e* 377 (M^+). An additional 0.12 g of the bis(*p*-nitrobenzoate) was isolated: NMR ($CDCl_3$) 3.20 (t, 2 H, *J* = 7 Hz), 4.57 (t, 2 H, *J* = 7 Hz), 7.2 (m, 10 H), and 8.3 ppm (m, 8 H). Upon stirring the mononitrobenzoate with excess active manganese dioxide in ether as in the preparation of **1a**, the corresponding ketone **1e** could be isolated.

References and Notes

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