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(22) Calculated from reactivities derived with the activation parameters given in ref 11. The derived relative reactivities (25°)[6] are 15.4, 3.93, 1.00, 0.061, and 0.069.

(23) π-delocalization parameters[15] other than $\sigma_R{}^+$ give poorer correlations: $\sigma_R{}^\circ$, $f = 0.082$; $\sigma_{R(BA)}$, $f = 0.106$; $\sigma_R{}^-$, $f = 0.19$.

(24) We intend to correct these deficiencies.

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(38) For a discussion of the uses and abuses of this expression, see ref 3, pp 153-156.

Excited State Interactions and Decay Routes in Bichromophoric Systems. Nonconjugated Phenyl Ketones[1]

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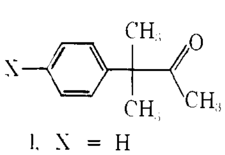
Abstract: The photoreactivity of a number of β-phenyl ketones possessing γ hydrogens has been investigated. In contrast to simple aliphatic ketones, these compounds undergo the type II photoelimination exclusively from the singlet, and in general this is the only significant photoreaction. Biacetyl and *cis*-1,3-pentadiene quenching were employed to determine singlet and triplet lifetimes and intersystem crossing yields, and thus rate parameters for the decay pathways in these compounds. Since both rates of the type II process and intersystem crossing are sensitive to substitution at phenyl, we infer that there is significant coupling between the two chromophores in the excited singlet state. Studies on somewhat geometrically restricted β-phenyl ketones indicate that coupling occurs through space rather than by a through-bond mechanism. Triplet states of these compounds have somewhat shorter lifetimes than those of typical aliphatic ketones but are, in contrast, completely unreactive in the type II process.

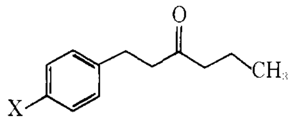
The photoreactivity of systems containing formally nonconjugated chromophores has been the subject of many recent investigations.[3] Among the processes which have been frequently observed are efficient intramolecular transfer of excitation, as evidenced by emission spectra and chemical reactions such as cis-trans isomerization,[4-11] intramolecular exciplex and excimer formation,[12-14] as well as reactions such as intramolecular cycloadditions.[3,15,16] One of the major questions that has not yet been satisfactorily resolved concerns the occurrence of modified excited states produced by interaction of dissimilar but energetically low-lying chromophores; such interactions occurring either by orbital overlap[17] or by through-bond coupling[18-20] have been the subject of both theoretical and spectroscopic investigation.

The present paper is concerned with the photochemical reactivity of some formally nonconjugated phenyl-carbonyl compounds. Since both simple aromatic compounds and aliphatic ketones, as well as the conjugated aryl ketones, have been rather extensively studied and their excited states fairly well characterized, it appeared likely that an investigation of systems with formally nonconjugated aromatic and carbonyl chromophores might readily reveal any excited-state interactions and permit their elucidation. Although both excited singlet and triplet states of aliphatic carbonyl compounds are lower in energy than those of most simple monocyclic aromatics, the energy spacing is small, particularly between triplet states such that considerable excitation migration or excited-state interaction might be anticipated. An attractive reaction for investigation of interactions between chromophores in nonconjugated phenyl ketones appeared to be the Norrish type II intramolecular photoelimination. This reaction, which has been extensively studied,[21] occurs fairly generally and with high efficiency for ketones having a γ C-H bond and lowest lying n,π* states. It has been previously shown that aliphatic ketones undergo the type II process from both singlet and triplet excited states,[22,23] Conjugated aromatic ketones react only from triplet states, presumably because rapid intersystem crossing deactivates the singlet before it can react. For phenyl ketones, the reaction is subject to strong substituent effects which have been attributed to mixing of ^{3}n,π* and $^3\pi,\pi$* states.[21,24]

Our preliminary investigations[25] of nonconjugated phenyl ketones included a study of the type II photoelimination in 4-methyl-4-phenyl-2-pentanone (MPP) (**1**) in which the carbonyl and phenyl chromophores are separated by a two-



1. X = H
2. X = Cl
3. X = Br
4. X = *t*-Bu
5. X = CN



6. X = H
7. X = Cl

carbon chain. Although absorption spectra of MPP show distinct carbonyl and phenyl transitions with very little indication of interaction, the photochemistry of MPP is quite different from that of both aliphatic and conjugated phenyl ketones. Although the type II process was the only reaction observed, a kinetic study showed that the reaction occurred with very low efficiency and only from excited singlet states of MPP. Although triplets of MPP were formed with moderate efficiency and had reasonable lifetimes, no reaction from the triplet could be detected. At approximately the same time these results were obtained, investigations by Stermitz[26,27] and by Wagner[28] (with other systems) revealed evidently related phenomena occurring with other compounds containing a carbonyl group with a β-phenyl substituent. Stermitz, *et al.*,[26,27] found that benzylacetone and benzylacetophenone are markedly resistant to photoreduction in 2-propanol, a reaction that normally proceeds with high efficiency for carbonyl compounds with lowest $^3n,\pi^*$ states. Wagner, *et al.*,[28] found that β-phenylbutyrophenone undergoes the type II process from the triplet with low efficiency but at a rate which is comparable to those of unsubstituted butyrophenones. It was suggested that the low efficiency in this case was due to a quenching process or intramolecular complex formation in competition with the normal reaction path.[28]

In this paper, we report an investigation of a series of β-phenyl ketones, including several compounds in which the phenyl group bears substituents, as well as two compounds in which the relative orientations of the two chromophores are restricted. A kinetic analysis of the results indicates that the two chromophores interact in the excited state such that the normal carbonyl photoreactivity is strongly modified; it appears that interchromophoric interactions are important for excited states of these and probably of other bichromophoric systems.

Experimental Section

General. Reagents for syntheses were obtained from either B & A Chemicals or Aldrich Chemical Co. and were used as received. Biacetyl for quenching studies was obtained from Aldrich and distilled before use. *cis*- and *trans*-1,3-pentadiene were obtained from Columbia Organics and distilled over lithium aluminum hydride before use.

Melting points were obtained on a Büchi apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, Ga. Nmr spectra were obtained on a Jeolco C60H1 spectrometer with TMS internal standard and infrared spectra on either a Perkin-Elmer 421 or 257 spectrometer. Ultraviolet spectra were recorded on a Unicam SP 800B instrument. Fluorescence and phosphorescence measurements were obtained on a Hitachi Perkin-Elmer MPF-2A spectrophotometer. Gas chromatographic analyses were performed on a Hewlett-Packard F&M 5750 instrument. A 15-ft 5% Apiezon L on Chromosorb G (60-80 mesh) column was used for analysis of ketone photoproducts, with tetralin added to each sample as an internal standard after the photolysis. Analyses of 1,3-pentadiene isomerizations were performed on a 35-ft 5% β,β'-oxydipropionitrile on a Chromosorb G (60-80 mesh) column, at room temperature (~25°) with a carrier flow rate of 5 ml/min.

4-Methyl-4-phenyl-2-pentanone[29,30] (1). In a 500-ml round-bottomed flask fitted with a magnetic stirrer were placed 45 g (0.34 mol) of anhydrous aluminum chloride and 100 ml of benzene. To this mixture was added dropwise, over a period of 1 hr, 25 g (0.25 mol) of mesityl oxide. The reaction mixture was stirred for 3 hr longer and then poured onto 150 g of crushed ice. The layers were separated, and the water layer was washed with three 50-ml portions of benzene. The organic layers were combined and washed with 25 ml of water, two 25-ml portions of 25% potassium carbonate solution, and 25 ml of water. The solution was dried over magnesium sulfate. Removal of the solvent and distillation of the residue afforded 30 g (68%) of a pale yellow oil: bp 124-125° (14 mm); ir (neat) 1715 cm^{-1}; nmr (CDCl$_3$) δ 7.25 (s, 5 H), 2.7 (s, 2 H), 1.8 (s, 3 H), 1.35 (s, 6 H).

The semicarbazone, white needles (ethanol), had mp 163-164°.

Anal. Calcd for $C_{13}H_{19}N_3O$: C, 66.64; H, 8.20; N, 17.93. Found: C, 67.00; H, 8.28; N, 17.98.

4-(4-Chlorophenyl)-4-methyl-2-pentanone (2). In a 500-ml round-bottomed flask cooled in a water bath were placed 56 g (0.5 mol) of chlorobenzene, 45 g (0.34 mol) of anhydrous aluminum chloride, and 25 ml of carbon disulfide. The mixture was stirred vigorously, while mesityl oxide (25 g, 0.25 mol) was added dropwise over a period of 1 hr. The stirring was continued for a period of 2 hr after addition was complete. At the end of that time, the reaction mixture was poured onto 100 g of ice and stirred until all ice was melted. The layers were separated, and the water layer was washed with three 100-ml portions of benzene. The organic extracts were combined and washed with two 100-ml portions of 25% potassium carbonate solution and 100 ml of water. The benzene solution was dried over magnesium sulfate and the solvent removed. Distillation of the residue gave 39.5 g (75%) of **2** as a pale yellow oil: bp 100-102° (0.25 mm); ir (neat) 1715 cm^{-1}.

The semicarbazone, white needles (ethanol), had mp 174-175°.

Anal. Calcd for $C_{13}H_{18}N_3OCl$: C, 58.32; H, 6.78; N, 15.69. Found: C, 58.30; H, 6.81; N, 15.77.

4-(4-Bromophenyl)-4-methyl-2-pentanone (3). Mesityl oxide (25 g, 0.25 mol), bromobenzene (79 g, 0.50 mol), and anhydrous aluminum chloride (45 g) were allowed to react in a similar manner in 50 ml of carbon disulfide to give, after the usual work-up, 110 g (85%) of **3** as a pale yellow oil: bp 135-140° (5 mm); ir (neat) 1715 cm^{-1}; nmr (CDCl$_3$) δ 7.26 (s, 4 H), 2.7 (s, 2 H), 1.8 (s, 3 H), 1.36 (s, 6 H).

The semicarbazone, white needles (ethanol), had mp 151-152°.

Anal. Calcd for $C_{13}H_{18}N_3OBr$: C, 50.01; H, 5.81; N, 13.46. Found: C, 50.09; H, 5.77; N, 13.38.

4-(4-Cyanophenyl)-4-methyl-2-pentanone (5). In a 300-ml round-bottomed flask equipped with reflux condenser and magnetic stirrer were placed 66 g (0.25 mol) of 4-(4-bromophenyl)-4-methyl-2-pentanone, 29.5 g (0.37 mol) of cuprous cyanide, and 45 ml of dimethylformamide. The mixture was stirred under reflux for 3 hr. At the end of that time, the reaction mixture was poured onto 200 ml of water containing 70 g of sodium cyanide. The mixture was stirred at room temperature for 0.5 hr. The layers were separated, and the aqueous layer was washed with three 100-ml portions of benzene. The organic layers were combined, washed with two 50-ml portions of 10% sodium cyanide solution, and dried over magnesium sulfate. Removal of the solvent followed by distillation gave 44.98 g (87%) of **4** as a colorless oil: bp 123-127° (0.5 mm); ir (neat) 1715 cm^{-1}; nmr (CDCl$_3$) δ 7.66 (m, 4 H), 2.90 (s, 2 H), 1.94 (s, 3 H), 1.39 (s, 6 H).

The semicarbazone, white needles (ethanol), had mp 149-150°.

Anal. Calcd for $C_{14}H_{18}N_4O$: C, 65.09; H, 7.02; N, 21.69. Found: C, 64.95; H, 7.16; N, 21.72.

4-(4-*tert*-Butylphenyl)-4-methyl-2-pentanone (4). A mixture of 16 g (0.09 mol) of 4-methyl-4-phenyl-2-pentanone and 12.6 g (0.14 mol) of *tert*-butyl chloride was stirred magnetically and cooled to 0° in an ice-salt bath. To this cooled mixture was added, in several portions, 10 g of anhydrous aluminum chloride. The reaction mixture was allowed to stir until all the ice in the cooling bath had melted and was then poured onto 25 g of ice. The mixture was extracted with three 25-ml portions of benzene. The organic layers were combined, washed with 25 ml of saturated potassium carbonate solution and 25 ml of water, and dried over magnesium sulfate. The solvent was removed and the product distilled, affording 7 g (33%) of **5** as a colorless oil: bp 110-120° (5 mm); ir (neat) 1715 cm^{-1}; nmr (CDCl$_3$) δ 7.39 (s, 4 H), 2.71 (s, 2 H), 1.72 (s, 3 H), 1.37 (s, 9 H), 1.29 (s, 6 H).

The semicarbazone, white plates (benzene), had mp 193–194°.

Anal. Calcd for $C_{17}H_{27}N_3O$: C, 70.55; H, 9.40; N, 14.52. Found: C, 70.41; H, 9.54; N, 14.59.

β-Phenylpropionyl Chloride. Hydrocinnamic acid (75 g, 0.5 mol) and 60 g (0.505 mol) of thionyl chloride were heated under reflux for 3 hr. Excess thionyl chloride was removed at aspirator pressure. The product was distilled at reduced pressure to give 64 g (76%) of a colorless oil, bp 110° (3.8 mm).

1-Phenyl-3-hexanone (6). The apparatus, consisting of a 2-l., three-necked flask fitted with mechanical stirrer, condenser, and dropping funnel, was dried overnight at 110°. In the flask were placed 12 g (0.5 g-atom) of magnesium turnings and sufficient ether to cover. A small amount of solution of 61.5 g of *n*-propyl bromide (0.5 mol) in 50 ml of anhydrous ether was introduced into the flask. Reaction began spontaneously, and stirring was begun while the remaining alkyl bromide solution was added at a rate sufficient to maintain reflux. The mixture was refluxed for 0.25 hr after addition was complete. To this solution was then added, in small portions, 91.2 g (0.5 mol) of anhydrous cadmium chloride. The mixture was refluxed for 0.5 hr, then the ether was removed by distillation, and 500 ml of benzene was added, with distillation continuing until the temperature of the distillate reached 75°. The condenser was connected again for reflux, and 250 ml more of benzene was added. After refluxing recommenced, a solution of 64 g (0.39 mol) of β-phenylpropionyl chloride in 100 ml of benzene was added over a period of 1.5 hr. The reaction mixture was refluxed for 4 hr and then allowed to cool. The white complex obtained was decomposed with 40% (v/v) hydrochloric acid solution. The organic layer was separated and the water layer washed with two 100-ml portions of benzene. The organic layers were combined, washed with 50 ml of water, three 50-ml portions of 25% potassium bicarbonate solution, and 50 ml of water, and then dried over magnesium sulfate. Removal of solvent, followed by distillation of the product, gave 42.1 g (62%) of a yellow oil: bp 150–151° (10 mm); ir (neat) 1720 cm^{-1}; nmr ($CDCl_3$) δ 7.18 (s, 5 H), 3.96 (t, 2 H), 2–3 (m, 5 H), 1.5 (m, 2 H), 1.86 (t, 3 H).

The 2,4-dinitrophenylhydrazone, orange crystals (ethyl acetate), had mp 172–173°.

Anal. Calcd for $C_{18}H_{20}N_4O_4$: C, 60.7; H, 5.64; N, 15.7. Found: C, 60.44; H, 5.68; N, 15.58.

***p*-Chlorohydrocinnamoyl Chloride.** The ethyl ester of *p*-chlorocinnamic acid was prepared by heating 100 g of the acid under reflux for 16 hr in 500 ml of absolute ethanol containing a small amount of *p*-toluenesulfonic acid. The solvent was removed by rotary evaporator. The ester was taken up in ethyl acetate and hydrogenated over 5% palladium on charcoal at 3 atm. After a quantitative amount of hydrogen had been taken up, the catalyst was removed by filtration and the solvent removed by rotary evaporator. The hydrogenated ester was heated under reflux with 40% potassium hydroxide for 0.5 hr and then acidified. The *p*-chlorohydrocinnamic acid was collected and recrystallized once from hexane. A mixture of 35 g (0.19 mol) of this acid and 80 g (0.42 mol) of thionyl chloride was heated under reflux with stirring for 3.5 hr. At the end of that time, excess thionyl chloride was removed on the rotary evaporator and the residue distilled at reduced pressure, affording 31.1 g (81%) of the acid chloride as a colorless oil.

***p*-Chloro-1-phenyl-3-hexanone (7).** The *n*-propylcadmium chloride was made as before, using 4.4 g of magnesium turnings (0.185 g-atom), 26 g of *n*-propyl bromide (0.19 mol), and 34.1 g of cadmium chloride (0.19 mol). As much ether as possible was removed by distillation and replaced by 400 ml of benzene. To the refluxing mixture of the organometallic compound in benzene was added, over a period of 40 min, 31.1 g (0.15 mol) of *p*-chlorohydrocinnamoyl chloride in 100 ml of benzene. Reflux was continued for 3 hr after addition was complete. Work-up as for 1-phenyl-3-hexanone, followed by distillation of the product, gave 21 g of (66%) *p*-chloro-1-phenyl-3-hexanone as a pale yellow oil: bp 125–135° (5 mm); ir (neat) 1707 cm^{-1}; nmr ($CDCl_3$) δ 7.15 (m, 4 H), 0.85 (t, 3 H), 1.5 (m, 2 H), 2.5 (m, 6 H).

The semicarbazone, white needles (benzene), had mp 136–137°.

Anal. Calcd for $C_{13}H_{18}N_3OCl$: C, 58.32; H, 6.78; N, 15.69. Found: C, 58.53; H, 6.93; N, 15.57.

***p*-Chlorobenzylacetone.** This compound was prepared in a similar manner from 14.0 g of *p*-chlorohydrocinnamoyl chloride and methylcadmium chloride, yield 4.2 g (33%) as a yellow oil.

The 2,4-dinitrophenylhydrazone, dark yellow powder (ethyl acetate), had mp 156.5–157.5°.

Anal. Calcd for $C_{16}H_{15}N_4O_4Cl$: C, 53.0; H, 4.1; N, 15.4. Found: C, 52.95; H, 4.21; N, 15.28.

2,2-Indandicarboxylic Acid. In a 3-liter, three-necked flask fitted with a magnetic stirrer were placed 270 g of absolute ethanol and 19 g (0.82 g-atom) of sodium metal which had been cut into small pieces. After solution of the sodium was complete, 750 ml of anhydrous ether was added, followed by 63 g (1.12 mol) of diethyl malonate. To this solution was added as quickly as possible 105 g (0.39 mol) of α,α′-dibromo-*o*-xylene in 750 ml of ether. The reaction mixture was stirred under reflux for 5 hr after addition was complete. The precipitate was allowed to settle and the solution filtered. The solvent was removed and the residue refluxed with 500 ml of water and 90 g of potassium hydroxide for 16 hr. At the end of that time, the solution was cooled and acidified with 30% (v/v) hydrochloric acid. The white diacid precipitate was collected and dried in a vacuum desiccator.

2-Indancarboxylic Acid. The diacid obtained from the previous reaction was placed in a beaker covered with aluminum foil and heated to 200° on a hot plate. The liquefied compound was held at 200° for 20 min, then allowed to cool. The product was recrystallized from *n*-heptane, affording 57 g (94% from dibromo-*o*-xylene) of the mono acid as white plates.

2-Indancarbonyl Chloride. A mixture of 19.8 g of 2-indancarboxylic acid and 50 ml of thionyl chloride was heated under reflux for 3 hr. The excess thionyl chloride was removed at reduced pressure and the product distilled at reduced pressure, affording 18.2 g (83%) of a colorless oil, bp 117–118° (2.6 mm).

2-Butanoylindan. An organocadmium reaction was carried out on 17.1 g of 2-indancarbonyl chloride in the manner previously described for 1-phenyl-3-hexanone, using 3.8 g of magnesium turnings (0.12 g-atom), 18.4 g (0.15 mol) of *n*-propyl bromide, and 27.2 g of anhydrous cadmium chloride. The ether used in the first stage of the reaction was replaced by 250 ml of benzene, and reflux was maintained for 5 hr. Work-up in the usual manner gave 12.6 g (75%) of 2-butanoylindan, bp 125–130° (1.5 mm).

The semicarbazone, white needles (benzene), had mp 148–149°.

Anal. Calcd for $C_{14}H_{19}N_3O$: C, 68.54; H, 7.81; N, 17.13. Found: C, 68.45; H, 7.87; N, 17.12.

2-Acetylindan. This compound was prepared in a similar manner, using 10 g (0.055 mol) of 2-indancarbonyl chloride, bp 140° (1 mm).

The oxime, white plates (methanol), had mp 124–125°.

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.5; N, 8.0. Found: C, 75.25; H, 7.67; N, 7.95.

1-Benzocyclobutenecarboxylic Acid. A 1.0-g (7.8 mmol) portion of 1-cyanobenzocyclobutene[31] was dissolved in 6 ml of KOH-saturated absolute ethanol and allowed to stand 24 hr at room temperature. Water (2 ml) was added and the solution refluxed 3 hr. The reaction mixture was diluted with 50 ml of water and the resultant suspension washed with ether. The aqueous phase was acidified with HCl and extracted with ether. The ether extracts were dried ($MgSO_4$), and the solvent was removed at reduced pressure. The residue was taken up in the minimum amount of hot 30–60° petroleum ether, and the solution was decanted from a small amount of insoluble oily material. Cooling to 10° precipitated 0.835 g (73%) of the desired acid, mp 72–73° (lit.[32] 74.5–76°).

1-Benzocyclobutenemethanol. A solution of 15.0 g (0.10 mol) of 1-benzocyclobutenecarboxylic acid in 75 ml of THF was added dropwise to a stirred slurry of 4.03 g (0.106 mol) of $LiAlH_4$ in 60 ml of THF. The mixture was stirred overnight at room temperature, decomposed by cautious dropwise addition of 4 ml of water, 4 ml of 15% NaOH, and 12 ml of water, and allowed to stir an additional 2 hr. The precipitated salts were removed by filtration and washed thoroughly with THF. Evaporation of the filtrate gave 11.1 g (82%) of crude alcohol, which was used without further purification. The analytical sample was purified by chromatography on alumina ($CHCl_3$) followed by bulb-to-bulb distillation: ir (neat) 3350 cm^{-1} (broad); nmr ($CDCl_3$) δ 7.0–7.6 (m, 4 H), 3.55–4.1 (m, 3 H), 3.39 (dd, $J = 4.5, |14|$ Hz, 1 H), 2.93 (dd, $J = 2.5, |14|$ Hz, 1 H), 2.30 (s, 1 H).

Anal. Calcd for $C_9H_{10}O$: C, 80.6; H, 7.5. Found: C, 80.41; H, 7.67.

1-Benzocyclobuteneacetonitrile. A solution of 9.6 g (72 mmol) of crude 1-benzocyclobutenemethanol and 27.3 g (143 mmol) of *p*-toluenesulfonyl chloride in 250 ml of dry pyridine was allowed to stand at 5° for 3 days. The mixture was poured into 1 l. of ice-water and extracted with ether. The ether extracts were washed with cold 6 *N* HCl, saturated $NaHCO_3$, water, and saturated NaCl and dried ($MgSO_4$). Removal of the ether at room temperature under reduced pressure gave 20.5 g of crude tosylate as a pale yellow viscous oil: ir (neat) 1170, 1185 cm^{-1}.

The crude tosylate was taken up in 60 ml of DMSO and added to a stirred suspension of 7.0 g (143 mmol) of NaCN in 90 ml of DMSO. The mixture was stirred overnight, poured into 1.5 l. of water to which several grams of $NaHCO_3$ had been added, and extracted with ether. The ether extracts were washed with water, saturated $NaHCO_3$, and saturated NaCl and dried ($MgSO_4$). Removal of the ether and short-path distillation of the residue gave 8.5 g (82%) of the desired nitrile as a colorless oil: bp 78–80° (0.1 mm); ir (neat) 2242, 990 cm^{-1}; nmr ($CDCl_3$) δ 7.3 (m, 4 H), 3.84 ($ABXY_2$, $J_{AB} = 5.5$, $J_{AX} = 2$, $J_{AY} = 7.5$ Hz, 1 H), 3.56 (ABX, $J_{AB} = 5.5$, $J_{AX} = |14.5|$ Hz, 1 H), 2.94 (dd, $J = 2, |14.5|$ Hz, 1 H), 2.74 (d, $J = 7.5$ Hz, 2 H).

Anal. Calcd for $C_{10}H_9N$: C, 83.9; H, 6.3; N, 9.8. Found: C, 83.71; H, 6.51; N, 9.73.

1-Benzocyclobuteneacetic Acid. This compound was prepared in a similar manner to 1-benzocyclobutenecarboxylic acid by dissolving 3.5 g (24 mmol) of the nitrile in 20 ml of KOH-saturated absolute ethanol. Work-up as described and recrystallization of the residue from 10 ml of hexane gave 3.0 g (76%) of the acid, mp 64–66° (lit.[33] 61.5–62.5°).

1-Benzocyclobuteneacetyl Chloride. A mixture of 4.76 g of 1-benzocyclobuteneacetic acid and 5.0 ml of thionyl chloride was heated gently (just below reflux) for 2 hr. The excess thionyl chloride was removed at reduced pressure and the residual oil distilled to give 5.0 g (94%) of the desired acid chloride as a colorless oil, bp 81–83° (0.5 mm).

1-(Benzocyclobutenyl)-2-pentanone (9). A solution of propylmagnesium bromide was prepared in the usual manner by addition of 1.50 g (12 mmol) of propyl bromide in 10 ml of anhydrous ether to 0.30 g (12 mmol) of Mg turnings suspended in 7 ml of ether. A total of 1.40 g (7.6 mmol) of anhydrous $CdCl_2$ was added in portions and the mixture refluxed 2.5 hr. The ether was removed by distillation and replaced with 20 ml of dry benzene. After refluxing 2 hr to ensure complete conversion to the propylcadmium, a solution of 1.50 g (8.3 mmol) of 1-benzocyclobuteneacetyl chloride in 10 ml of benzene was added dropwise and the resultant mixture refluxed overnight. After the mixture was cooled, 15 ml of 15% HCl was added dropwise and the two-phase system stirred 2 hr at room temperature. The layers were separated, and the aqueous phase was extracted with benzene. The benzene layers were washed with water, saturated $NaHCO_3$, and saturated NaCl and dried ($MgSO_4$). Removal of the benzene at reduced pressure and kugelrohr distillation of the residue [~140° (0.5 mm)] gave 1.06 g of a colorless oil consisting of three components in a ratio of approximately 1:6:20 by glpc. The desired ketone was isolated as the semicarbazone by treating 1.0 g of the distillate with 10 ml of hot aqueous ethanol containing 1.0 g of semicarbazide hydrochloride and 1.5 g of sodium acetate. The semicarbazone, which crystallized out upon cooling, was collected by filtration and recrystallized from aqueous ethanol to give 0.33 g of pure semicarbazone, mp 127–128.5°.

Anal. Calcd for $C_{14}H_{19}N_3O$: C, 68.5; H, 7.8; N, 17.1. Found: C, 68.48; H, 7.65; N, 17.06.

The ketone was regenerated by steam distillation of a mixture of 1.04 g of semicarbazone and 2.0 g of phthalic anhydride. The total distillate was extracted with benzene, and the benzene extracts were washed and dried as usual. Removal of the benzene and kugelrohr distillation of the residue gave 0.74 g of the desired ketone as a colorless oil: ir (neat) 1710, 997 cm^{-1}; nmr ($CDCl_3$) δ 7.25 (m, 4 H), 3.93 ($ABXY_2$, $J_{AB} = 5.5$, $J_{AX} = 2.5$, $J_{AY} = 7.5$ Hz, 1 H), 3.51 (ABX, $J_{AB} = 5.5$, $J_{AX} = |14|$ Hz, 1 H), 2.87 (d, $J = 7.5$ Hz, 2 H), 2.75 (dd, $J = 2.5, |14|$ Hz. 1 H), 2.47 (broad tr, 2 H), 1.69 (m, 2 H), 0.93 (tr, 3 H).

1-(Benzocyclobutenyl)acetone. A solution of 1.0 g (7 mmol) of 1-benzocyclobuteneacetonitrile in 15 ml of ether was added dropwise to an ice-cooled solution of methylmagnesium iodide prepared from 1.5 g (11 mmol) of methyl iodide and 0.24 g (10 mmol) of Mg turnings in 25 ml of ether. After the solution was stirred overnight at room temperature, 15 ml of water and 3 ml of 33% H_2SO_4 were added dropwise, and the two-phase system was stirred vigorously for 1 hr. The aqueous phase was extracted with ether, and the ether layers were washed and dried as usual. Removal of the ether gave 0.5 g of a yellow oil which was converted to the semicarbazone as described for **9.** Recrystallization from ethanol gave 0.28 g of semicarbazone, mp 188–190.5°.

Anal. Calcd for $C_{12}H_{15}N_3O$: C, 66.3; H, 7.0; N 19.3. Found: C, 66.49; H, 7.04; N, 19.14.

The ketone was regenerated from the semicarbazone (0.26 g) by steam distillation in the presence of phthalic anhydride as described for **9.** Kugelrohr distillation [~110° (0.5 mm)] gave 0.19 g of ketone as a colorless oil: ir (neat) 1710, 996 cm^{-1}; nmr ($CDCl_3$) 7.23 (m, 4 H), 3.91 ($ABXY_2$, $J_{AB} = 5.5$, $J_{AX} = 2.5$, $J_{AY} = 7.5$ Hz, 1 H), 3.50 (ABX, $J_{AB} = 5.5$, $J_{AX} = |14|$ Hz, 1 H), 2.90 (d, $J = 7.5$ Hz, 2 H), 2.79 (dd, $J = 2.5, |14|$ Hz, 1 H), 2.23 (s, 3 H).

Photochemical Studies. The solvent used in all cases was benzene (99.99% pure, obtained from James Hinton through Columbia Organic Chemicals) unless otherwise specified. Ketone concentrations were adjusted so that the ketone absorbed greater than 99% of the incident light. Ketone purity was 99.0% as determined by gas chromatography. Pure samples of the methyl aryl pentanones, indanyl propyl ketone, 1-benzocyclobutenyl-2-pentanone, and *p*-chloro-1-phenyl-3-hexanone were obtained by preparation and repeated crystallization of the semicarbazones followed by steam distillation of the semicarbazone in the presence of phthalic anhydride, followed by further distillation of the regenerated ketone. Pure 1-phenyl-3-hexanone was obtained *via* spinning band distillation of the ketone at 0.1 mm pressure.

Samples (4 ml) were prepared in 13 × 100 mm Pyrex test tubes which had previously been constricted about 1 cm from the lip. These samples were subjected to three freeze-pump-thaw cycles on a vacuum line and sealed at 5×10^{-5} mm. Irradiations at 313 nm were carried out in a merry-go-around apparatus, using a Hanovia medium-pressure 450-W mercury lamp.

Filters to isolate the 313-nm line consisted of Dow-Corning 7-54 glass windows and 1 cm of a solution of 138 g of $NiSO_4 \cdot 6H_2O$ and 42 g of $CoSO_4 \cdot 7H_2O$ in 300 ml of water. Irradiations at 313 nm were generally run for approximately 24 hr. Irradiations at 254 nm involved a low-pressure mercury arc filtered through 1 cm of the following solution: 112.5 g of $NiSO_4 \cdot 6H_2O$, 75 g of $CoSO_4 \cdot 7H_2O$, and 0.044 g of 2,7-dimethyl-3,6-diazacycloheptadiene perchlorate in 250 ml of water. Spectrograde hexane was used as solvent in these irradiations, and a quartz filter well was used.

Light intensities were in general measured using ferrioxalate actinometry.[34,35] Stilbene used as an actinometer gave similar results. Reaction products were analyzed by gas chromatography. In the case of 1-phenyl-3-hexanone and *p*-chloro-1-phenyl-3-hexanone, quantum yields in the biacetyl quenching experiment were determined relative to 4-methyl-4-phenyl-2-pentanone as actinometer.

Results

Para-Substituted 4-Methyl-4-phenyl-2-pentanones. The substituted compounds **2–5** were prepared as described in the Experimental Section by a Friedel-Crafts reaction. Spectra of the three compounds **2, 4,** and **5** whose photochemistry was extensively investigated are compared with those of the parent compound **1** and other β-phenyl ketones in Table I. In each case, the long-wavelength ultraviolet region shows prominent carbonyl and aromatic transitions which, except for the *p*-cyano compound **4**, are not substantially altered from the corresponding transitions in the parent compound **1.** None of the compounds investigated were found to show emission in room temperature solutions in benzene. However, all the compounds studied showed relatively strong phosphorescence in EPA glass at 77°K; approximate triplet energies estimated from the phosphorescence onset are given in Table I. Although some of these values appear high considering the chromophores involved, special significance should probably not be attached to them in terms of the room-temperature solution photochemistry since the phosphorescence may occur from specific conformations trapped in the 77°K glass.

Preliminary irradiation studies in benzene showed that

Table I. Spectral Data for β-Phenyl Ketones

Compd	λ_{max}, nm (ϵ) CO	λ_{max}, nm (ϵ) Ar	E_T, kcal/mol
4-Methyl-4-phenyl-2-pentanone (**1**)	290 (32)	258 (214)	77.9
4-(4-Chlorophenyl)-4-methyl-2-pentanone (**2**)	295 (31)	268 (312)	81.5
4-(4-*tert*-Butylphenyl)-4-methyl-2-pentanone (**4**)	300 (37)	258 (688)	80.3
4-(4-Cyanophenyl)-4-methyl-2-pentanone (**5**)	290 (143)	274 (600)	77.8
1-Phenyl-3-hexanone (**6**)	290 (30)	260 (198)	85.3
1-(*p*-Chlorophenyl)-3-hexanone (**7**)	295 (38)	271 (344)	83.6
2-Butanoylindan (**8**)	290 sh (26)	274 (810) 269 (700) 261 (450)	79.0
1-(Benzocyclobutenyl)-2-pentanone (**9**)	290 sh (40)	271 (1790) 264 (1960) 259 (1235)	

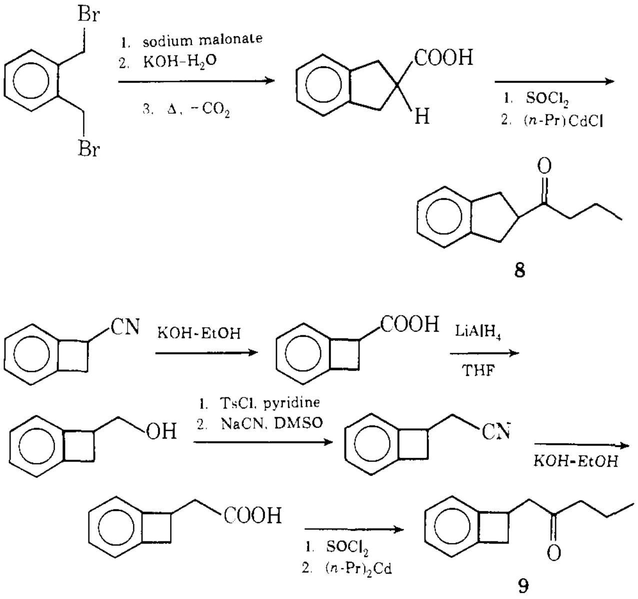
compounds **2, 4,** and **5** undergo the Norrish type II reaction to yield acetone and the substituted α-methylstyrene as their only major photoreaction. The bromo compound **3** was found to yield several unidentified products on irradiation; since bromo compounds have been previously reported to undergo several reactions involving release of bromine atoms, it was decided not to pursue further a study of its reactivity. Reaction efficiencies in quenching processes for compounds **1, 2, 4,** and **5** were investigated by following the production of the substituted α-methylstyrene as well as the disappearance of the starting ketone by vpc. Quantum yields for the type II reaction for these compounds in benzene are listed in Table II. Although an extensive investigation of solvent effects for all the compounds was not conducted, limited investigations indicated that reactivity is largely unaffected by change in solvent. For example, the reactivity of **1** was found to be the same within experimental error in hexane as in benzene. In addition, **1** and the *p*-chloro compound **2** were both found to react with the same quantum efficiencies for the type II process in benzene and acetonitrile.

The reactivity of **1, 2, 4,** and **5** was also investigated in the presence of varying concentrations of *cis*- and *trans*-1,3-pentadiene. No quenching of the type II process occurred for any of the compounds at concentrations up to 1 *M* 1,3-pentadiene; however, sensitization of the cis → trans isomerization of 1,3-pentadiene was observed. Good plots of $1/\phi_{c\to t}$ *vs.* 1/[1,3-pentadiene] were obtained for all compounds except **4**, and from these plots the triplet lifetimes and values of ϕ_{isc}, the quantum yield for intersystem crossing, were obtained. In the case of **4** the reciprocal plot showed two distinct linear portions with a sharp break, suggesting the presence in this compound of two nonequilibrating (perhaps consecutive) triplets. Values determined for ϕ_{isc} and the triplet lifetimes are listed in Table II. Biacetyl, which has been found to quench singlets of ketones and a variety of other compounds at diffusion-controlled rates,[36,37] was also investigated as a potential quencher for the type II reaction of **1–5**. For each compound, biacetyl was found to quench the type II process, and good linear Stern–Volmer plots were obtained; the rather widely differing values obtained from the slopes of these plots are also listed in Table II.

1-Phenyl-3-hexanone and *p*-Chloro-1-phenyl-3-hexanone. The two linear ketones were synthesized by condensation of *n*-propylcadmium chloride with 3-phenylpropionyl chloride and 3-(4-chlorophenyl)propionyl chloride, respectively. Spectral data for these compounds, **6** and **7**, are given in Table I. Both of these compounds were found to undergo the type II process as their major reaction on direct irradiation, although **7** was found to give a variety of additional products. Experiments with 1,3-pentadiene and biacetyl led to results qualitatively similar to those for the MMP's. Data obtained from the ketone-sensitized 1,3-pentadiene isomerization and quenching of the type II process by biacetyl are given in Table II as are the quantum yields for the process in the absence of quenching.

Rigid Ketones. The stereochemically somewhat rigid ketones **8** and **9** were synthesized as outlined in Scheme I. As with the other β-phenyl ketones, clearly resolvable aromatic and carbonyl transitions are present in the electronic spectra of these compounds (Table I). Both of these compounds undergo the type II process on direct irradiation. An additional product, quenchable by 1,3-pentadiene, was formed from **9**. This unidentified product, formed with low efficiency ($\phi \sim 0.005$), had a retention time slightly longer than the starting ketone and perhaps could be the product arising from intramolecular abstraction of a cyclobutenyl hydrogen. Quantum yield and quenching data for **8** and **9** are summarized in Table II. The **9**-sensitized 1,3-pentadiene isomerization exhibited two-component behavior similar to that observed with **4**.

Scheme I



Discussion

Although ketones **1–9** undergo the type II process as has been observed for other alkyl ketones and aryl alkyl ketones possessing γ hydrogens, there are striking differences for the β-phenyl-substituted ketones. As a group, compounds **1–9** stand out from other ketones bearing γ hydrogens in that (a) reaction occurs only from excited singlet states, even though triplets are formed in the direct irradiation and live long enough to react, (b) rates of the type II process from excited singlets of **1–9** vary widely and are extremely sensitive to substituents on the phenyl ring, and (c) rates of intersystem crossing from excited singlets vary quite widely and are also sensitive to substitution on the phenyl ring. These differences may be easily recognized by comparing rate data for ketones **1–9** with those for 2-pentanone[38] listed in Table III. These data are obtained from the measured kinetic data in Table II as follows. The observed results can be accounted for by eq 1–8. Assuming biacetyl quenches singlet excited states, K^{1*}, with a rate constant $k_{qs} = k_{diff} =$

Table II. Quantum Yield and Lifetime Data for β-Phenyl Ketones

Compd	ϕ_{II}	$\phi_{II}{}^s$	Biacetyl slope, M^{-1}	$\tau_s \times 10^9$, sec	ϕ_{isc}	$\tau_t \times 10^9$, sec
2-Pentanone[a]	0.30	0.025		2.0	0.63	78
4-Methyl-4-phenyl-2-pentanone (**1**)	0.02	0.02	22.6	4.5	0.15	23
4-(4-Chlorophenyl)-4-methyl-2-pentanone (**2**)	0.14	0.14	0.49	0.09	0.12	7.3
4-(4-*tert*-Butylphenyl)-4-methyl-2-pentanone (**4**)	0.19	0.19	2.04	0.4	0.76	7.5
4-(4-Cyanophenyl)-4-methyl-2-pentanone (**5**)	0.17	0.17	1.49	0.3	0.33	15
1-Phenyl-3-hexanone (**6**)	0.0016	0.0016	79.0	15.8	0.14	9.8
1-(*p*-Chlorophenyl)-3-hexanone (**7**)	0.0005	0.0005	2.53	0.51	0.095	13.5
2-Butanoylindan (**8**)	0.048	0.048	172	34.3	0.034	21
1-(Benzocyclobutenyl)-2-pentanone (**9**)	0.0058	0.0058	7.4	1.5	0.46	6.0

[a] Data from ref 21 and 23.

Table III. Kinetic Parameters for β-Phenyl Ketone Excited States

Compd	$k_{II}{}^s \times 10^{-7}$, $\sec^{-1}$	$k_{isc} \times 10^{-7}$, $\sec^{-1}$	$k_d{}^s \times 10^{-7}$, $\sec^{-1}$	$1/\tau_t \times 10^{-7}$, $\sec^{-1}$
2-Pentanone[a]	1.2	31	18	13
4-Methyl-4-phenyl-2-pentanone (**1**)	0.4	3.3	18	43
4-(4-Chlorophenyl)-4-methyl-2-pentanone (**2**)	160	130	820	140
4-(4-*tert*-Butylphenyl)-4-methyl-2-pentanone (**4**)	47	190	>12	130
4-(4-Cyanophenyl)-4-methyl-2-pentanone (**5**)	57	110	170	67
1-Phenyl-3-hexanone (**6**)	0.01	0.89	5.4	100
1-(*p*-Chlorophenyl)-3-hexanone (**7**)	0.1	19	180	74
2-Butanoylindan (**8**)	0.14	0.1	2.7	84
1-(Benzocyclobutenyl)-2-pentanone (**9**)	0.4	30	36	170

[a] Data from ref 21 and 23.

$$\mathrm{K} \longrightarrow \mathrm{K}^{1*} \qquad (1)$$

$$\mathrm{K}^{1*} \xrightarrow{k_{II}} \text{“BR”} \longrightarrow \text{products} + \mathrm{K}^0 \qquad (2)$$

$$\mathrm{K}^{1*} \xrightarrow{k_{isc}} \mathrm{K}^{3*} \qquad (3)$$

$$\mathrm{K}^{1*} \xrightarrow{k_d} \mathrm{K}^0 \qquad (4)$$

$$\mathrm{K}^{1*} + \mathrm{B} \xrightarrow{k_{qs}} \mathrm{B}^{1*} + \mathrm{K}^0 \qquad (5)$$

$$\mathrm{K}^{3*} \xrightarrow{\tau_t^{-1}} \mathrm{K}^0 \qquad (6)$$

$$\mathrm{K}^{3+} + \mathrm{P} \xrightarrow{k_{qt}} \mathrm{P}^{3*} + \mathrm{K}^0 \qquad (7)$$

$$\mathrm{P}^{3*} \longrightarrow \alpha(\mathrm{P}^1) + (1 - \alpha)\mathrm{P} \qquad (8)$$

$5 \times 10^9\ M^{-1}\ \sec^{-1}$,[41] lifetimes for K^1*, τ_s, can be obtained, and from these lifetimes rate constants for the type II process can be estimated by eq 9. These k_{II} values must be regarded as minimum values since an appreciable fraction of the ketone singlets reacting *via* eq 2 may return to the starting ketone.[42] Values for the triplet lifetimes (τ_t) and yields (ϕ_{isc}) are obtained from the ketone triplet sensitized 1,3-pentadiene isomerization, and k_{isc} values are obtained from eq 10.

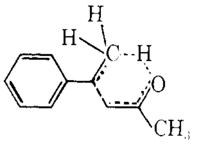
$$k_{II} = \phi_{II}/\tau_s \qquad (9)$$

$$k_{isc} = \phi_{isc}/\tau_s \qquad (10)$$

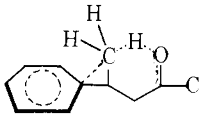
Since the sum of $\phi_{II} + \phi_{isc}$ is generally far from unity, it is evident that an additional process is deactivating excited singlets of these ketones, even allowing for considerable return of the intermediate biradical in eq 2 to starting material. Since ϕ_{II} is generally small for most compounds, ignoring return to starting ketone enables estimation of the efficiency of the deactivation process by eq 11. The rate of this process may be further estimated as $k_d = \phi_d/\tau_s$. From the values listed in Table III, it may be seen that this deactivation is a major pathway for most of the β-phenyl ketones, and one which accounts for over 80% of the excited singlets in all except **2**, **4**, **5**, and **9**.

$$\phi_d = 1 - \phi_{isc} - \phi_{II} \qquad (11)$$

Type II Reactivity. One of the most interesting results of this investigation is the wide variation observed in relative values for k_{II} for the ketones **1–9**. Perhaps most striking are the values for the substituted MPP's which vary over a range of almost three orders of magnitude and for which all except the parent MPP have faster rate constants than that for the reference compound 2-pentanone. The apparent activation of ketones **2**, **4**, and **5** by the substituted β-phenyl group compared with 2-pentanone is surprising and a little puzzling, particularly since the similarly substituted β-phenyl ketones **6** and **7** show much lower reactivity than 2-pentanone. Clearly the acceleration of k_{II} by the various para substituents is too large to be attributed solely to changes in the biradical partitioning (*vide infra*), especially since the singlet lifetimes are much shorter in ketones **2**, **4**, and **5** than for 2-pentanone. We envision two potential explanations for the enhancement of k_{II} in these compounds. If hydrogen abstraction and cleavage are a synchronous process, the energy of a transition state such as **10** might be expected to be strongly influenced both by the phenyl and by its para substituents. Alternatively, if a biradical is formed as an intermediate, the reactivity of the γ hydrogen might also be influenced by substitution at phenyl. As transition state **11** indicates, it might be possible that a "homo-benzylic" stabilization occurs.[43] The observation that groups both electron withdrawing (*p*-CN) and electron donating (*p-t*-Bu) relative to hydrogen enhance rates for the reaction is in line with observations for other processes involving radical stabilization.[44] However, the effect of substituents, especially the *p-t*-Bu group, appears somewhat larger than would be expected. The importance of stabilization of developing radicals such as **11** appears questionable. Although a modest para-substituent effect is observed, data from hydrogen abstraction studies show no enhanced reactivity of the methyl hydrogens of substituted *tert*-butylbenzenes.[45] In contrast to the MPP's, there is no opportunity for special phenyl stabilization for **6–9**, and for these ketones k_{II} is much lower than for the reference compound 2-pentanone. Therefore the primary effect of β-phenyl substitution on carbonyl photoreactivity appears to be rather clearly a



10



11

deactivating one. In **1**, a near cancellation of the basic phenyl-carbonyl deactivation by the phenyl-β-hydrogen activation gives a k_{II} close to that for 2-pentanone, while in the substituted MPP's the activation evidently overwhelms the deactivating process.

The deactivation process is nonetheless a significant interaction since k_{II} for **6** is less than 1% of k_{II} for 2-pentanone. Furthermore, even when the β-hydrogen activation is removed as in **6** and **7**, k_{II} values for the two compounds clearly show that substitution on phenyl can rather appreciably affect carbonyl reactivity. In this case, substitution of *p*-Cl for hydrogen on phenyl gives rise to a tenfold activation of the carbonyl group in the type II process. These results suggest then that the two chromophores, which apparently interact very little in the ground state as evidenced by the spectroscopic transitions, interact much more strongly in the excited singlet state. Although the apparent consequence of β-phenyl substitution is a lowering of the typical carbonyl n,π^* excited state reactivity, the large effect of substitution at phenyl on photoreactivity suggests that there is some basis for considering the lowest excited state as being largely a delocalized excited state involving both chromophores.

Up to this point we have specifically neglected partitioning in the singlet biradical (return *vs.* reaction) as an explanation for the variation in k_{II}. For the branched ketones **1–5**, it is quite possible that substitution at phenyl may not only facilitate biradical formation but also stabilize the biradical intermediate. This could certainly result in different partitioning factors for the various substituents. For the ketones **6–9** where abstraction occurs from the remote methyl group, we would anticipate only minor, if any, differences in the partitioning ratio.

Through-Bond *vs.* Through-Space Coupling. Rigid Systems. Potentially, coupling between the two chromophores can occur either *via* through-space or through-bond mechanisms. Through-space interactions would at first seem rather unlikely since the type II process does not normally seem to be strongly quenched in benzene solution. However, recent evidence suggests that new solvent-specific decay routes are available to ketone n,π^* triplets in aromatic solvents.[46,47] Moreover, since intramolecular processes are frequently greatly facilitated over the corresponding intermolecular reactions for entropic reasons, it might be anticipated that effects not observable in the bimolecular case might become important in a bichromophoric system. The second possibility, through-bond coupling, should be distinguishable from the former in rigid systems because of the rather specific alignment required for this type of coupling to be effective.[18-20]

In order to determine the nature of the β-phenyl-carbonyl interaction, we studied semirigid systems in which steric constraints should maintain the phenyl and carbonyl in relatively fixed arrangements. Molecular models indicate that in the indanyl propyl ketone **8** the C_α–C_β bond is nearly parallel with the ring, and rather minimal through-bond coupling would be anticipated. In contrast, models suggest that the C_α–C_β bond in the benzocyclobutenyl ketone **9** should be nearly perpendicular to the ring and the plane of the carbonyl group and thus aligned such as to maximize through-bond coupling of the two chromophores.

Both ketones **8** and **9** show type II abstraction from the remote methyl group only from their excited singlet states. However, compared with the reference β-phenyl ketone **6** these both show greatly enhanced reactivity (factors of 14 and 40, respectively). The relative k_{II}^{s} values for **8** and **9** are still somewhat lower than that for 2-pentanone, but the retarding effect of the β-phenyl has clearly been diminished.[48] Nonetheless, the fact that rates for **8** and **9** are not very different from each other suggests strongly that a through-bond coupling cannot account for the phenyl-carbonyl interaction. A more consistent interpretation of these results is that the two chromophores couple by a through-space interaction, and that in **8** and **9** the semirigid geometry does not permit the two chromophores to explore as many orientations as are available to the open chain compounds such as **6** and **7**.

Intersystem Crossing in the β-Phenyl Ketones. The intersystem crossing data for ketones **1–9** provide additional strong evidence that the chromophores are coupled in the excited singlet state. The general trend in the k_{isc} values is similar to that observed for k_{II}^{s}. The intersystem crossing data are potentially much more revealing than the type II data since k_{isc} values should be unaffected by partitioning (if any) in the type II biradical. Concentrating on ketones **1** and **6–9**, it appears that in general the effect of phenyl substitution is again a deactivating one, relative to 2-pentanone, and k_{isc} varies much in the same manner as k_{II}^{s}. Since the carbonyl-like absorption occurs at longest wavelength, the β-phenyl substitution should introduce into the molecules a π–π^* triplet state intermediate in energy between the ketone n–π^* singlet and triplet states, the net result on k_{isc}, if the chromophores were uncoupled, should be an undiminished rate or perhaps an enhanced rate of intersystem crossing due to new paths or to mixing in the triplet state.[49] These intersystem crossing data, therefore, also point toward the presence of coupling in the excited singlet state. In contrast, the enhanced type II reactivity of **2**, **4**, and **5** relative to **1** is accompanied by an enhancement of k_{isc}. The most general explanation is that intersystem crossing and the type II abstraction are intimately related to each other and to the interchromophoric coupling. Since the final states which provide the nonradiative continuum for intersystem crossing and type II processes are different, similarities in k_{II}^{s} and k_{isc} are more readily attributable to similarities in electronic factors in the initial state.[50] An attractive model is one in which intersystem crossing from the singlet state of the coupled chromophores is induced by distortions along a type II potential surface.

Other Nonradiative Decay Paths from Excited Singlets. In several cases, the low values for the sum of the type II quantum efficiencies and the intersystem crossing yields make it clear that a considerable fraction of the excited singlets formed on direct irradiation is deactivated by other nonradiative pathways. Values for these rate constants, k_{d}^{s}, are tabulated in Table III. While it is difficult to assign these rates to a specific process, it is noteworthy that several of the β-phenyl ketones have accelerated k_{d}'s relative to 2-pentanone. Unsubstituted or *p*-alkyl derivatives have about the same values, and there is no large effect for semirigid compounds **8** and **9**. However, *p*-chloro and *p*-cyano compounds **2**, **5**, and **7** are markedly accelerated. Once again the strong influence observed on what are essentially carbonyl excited-state processes introduced by substituents on the phenyl underlines the interchromophoric interaction; the direction of the effect is reasonable since aromatic nitriles and chloroaromatics have notably short singlet lifetimes.[51]

An alternative explanation might include consideration of specific β-phenyl–carbonyl interactions which could be enhanced by electron-withdrawing substituents on phenyl. This would point to π-carbonyl–π-phenyl interactions as a possible mechanism for the coupling. In **8**, such interaction is restricted, yet the k_{II}^{s} and $_{\text{isc}}$ values for **8** imply strongly the operation of considerable interchromophoric coupling. A recent study[52] that seems to bear closely on the present results concerns the investigation of the photoreactivity of the isomeric 2-acetylbenzonorbornenes. The exo isomer, in which close approach of the carbonyl group to phenyl is prohibited, undergoes a type I cleavage, apparently from the triplet state, with a quantum efficiency of 0.015. The triplet state of this compound is formed with high efficiency. In contrast, the endo isomer is photostable and gives only a low yield of triplet states. The authors suggest that in the endo isomer close approach of the carbonyl n orbital to the π orbitals of the aromatic system provides a channel for rapid radiationless deactivation. In fact, both n-carbonyl-π-phenyl and π-carbonyl-π-phenyl interactions may be important mechanisms for coupling of the chromophores.

Enhanced nonradiative decay from singlets of bichromophoric systems where one of the components is a carbonyl and where close approach of the chromophores is possible appears to be a fairly general phenomenon. Kurowsky and Morrison[53] have recently observed enhanced $k_d{}^s$ in 5-hepten-2-ones along with inefficient intersystem crossing; in these compounds, however, unlike ketones **1–9**, type II reactivity is completely lacking, and the authors suggest formation of an intramolecular singlet exciplex best explains both the products ultimately formed and the enhanced deactivation.[54]

Triplet Lifetimes and (Lack of) Reactivity. Rather surprisingly triplets of **1–9** are inactive in the type II reaction, even though yields of triplets and lifetimes are sufficient to permit typical ketone ^{3}n-π^* reactivity to be observed. In particular compounds such as **5**, the lack of reactivity could be due to a lowest lying aromatic triplet. However, this is not a compelling rationalization in all cases, and it appears likely that there is considerable interchromophoric coupling in the triplet manifold as well as the singlet. Such a through-space coupling has been proposed by Wagner[28] and by Stermitz[26] to explain the lack of carbonyl reactivity in β-phenyl aromatic ketones in which the uncoupled ketone triplet is surely lower than the phenyl triplet. The deactivating interaction here may well be related to the quenching of benzophenone triplets by substituted benzene solvents reported by Schuster, *et al.*[46,47] The lack of clear-cut trends in substituent effects may, however, indicate that other factors are important.

Summary

We find that, in contrast to simple aliphatic ketones, β-phenyl ketones undergo the type II photoelimination exclusively from the singlet, and in general this is the only significant photoreaction. Since rates of the type II process, intersystem crossing, and internal conversion are all sensitive to substituents on the phenyl, we infer that there is significant coupling between the two chromophores in the excited singlet state. From trends in the substituent effects and data on the reactivity of **8** and **9**, the geometrically restricted systems, we conclude that the coupling occurs through space rather than by a through-bond mechanism. The lack of reactivity of triplet states of these compounds also points to significant interchromophoric coupling in the triplet manifold.

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