17.1, 15.6, 140.0, 9.7; IR ($CHCl_3$) ν 2900, 2830, 2210, 1690, 1430, 1305, 1130, 1055, 1020, 980, 895 cm^{-1}; MS (CI), m/e 357 (MH^+); MS (EI), m/e (relative intensity) 355 (11), 297 (21), 283 (100), 271 (91), 253 (15), 245 (25), 213 (44), 201 (58), 157 (15), 85 (100).

(*Z*,*Z*,*Z*,*Z*)-1-(Tetrahydropyranyloxy)-4,7,10,13-nonadecatetraene (12). By use of a procedure identical with that described for the preparation of **4**, compound **11** (1.0 g, 2.8 mmol) in absolute EtOH (5 mL) was hydrogenated over P-2 Ni, prepared via sodium borohydride reduction of $Ni(OAc)_2{\cdot}4H_2O$ (0.7 g, 2.8 mmol) in absolute EtOH (15 mL). Hydrogen uptake was quantitative in 5 h. Workup followed by flash chromatography (hexane/2% ether) gave 680 mg (65%) of tetraene **12** as a colorless oil (purity >95% by GC): ^1H NMR δ 0.89 (t, J = 6.9 Hz, 3 H, CH_3), 1.19–1.44 (m, 6 H, alkyls), 1.95–2.24 (m, 4 H, $C{=}CCH_2$), 2.70–2.92 (m, 6 H, $C{=}CCH_2C{=}C$), 3.33–3.89 (m, 4 H, OCH_2), 4.58 (t, J = 3.4 Hz, 1 H, OCHO), 5.27–5.48 (m, 8 H, vinyl); ^{13}C NMR δ 130.2, 129.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.4, 98.6, 66.7, 62.0, 31.4, 30.6, 29.5, 29.2, 27.1, 25.5, 25.4, 23.8, 22.5, 19.4, 14.0; IR ($CHCl_3$) ν 2830, 2720, 2650, 1650, 1445, 1370, 1345, 1320, 1255, 1115, 1070, 1020, 990, 970, 900, 865 cm^{-1}; MS (CI); m/e 361 (MH^+); MS (EI), m/e (relative intensity) 360 (5), 276 (8), 150 (44), 95 (100).

(*Z*,*Z*,*Z*,*Z*)-1-Bromo-4,7,10,13-nonadecatetraene (13). To a solution of triphenylphosphine (0.94 g, 3.6 mmol) in dry CH_2Cl_2 (0.6 mL) at 0 °C was added dropwise a solution of CBr_4 (0.59 g, 1.8 mmol) in dry CH_2Cl_2. After 10 min at 0 °C, the reaction mixture was warmed to room temperature over 45 min and then cooled to 0 °C, and **12** (0.25 g, 0.7 mmol) in CH_2Cl_2 (1 mL) was added. The resulting mixture was warmed to room temperature and stirred for 10 min. The triphenyl phosphite was precipitated by addition of hexane (20 mL). After filtration, the organic extracts were washed with sodium bicarbonate (20 mL) and brine (20 mL), then dried (Na_2SO_4), and concentrated. Purification of the residue on silica gel (pentane) gave 0.17 g (76%) of bromide **13** as a colorless liquid (purity >95% by GC): ^1H NMR δ 0.90 (t, J = 6.7 Hz, 3 H, CH_3), 1.10–1.44 (m, 6 H, alkyls), 1.80–2.17 (m, 4 H, CH_2CH_2Br + $C{=}CCH_2$), 2.35 (apparent q, J = 7.0 Hz, 2 H, $C{=}CCH_2$), 2.89–2.71 (m, 6 H, $C{=}CCH_2C{=}C$), 3.42 (t, J = 6.6 Hz, 2 H, CH_2Br), 5.20–5.48 (m, 8 H, vinyl); ^{13}C NMR δ 130.5, 129.5, 128.7, 128.4, 128.0, 127.9, 127.8, 127.5, 34.1, 33.4, 32.5, 31.5, 29.3, 27.2, 25.7, 25.5, 22.3; IR ($CHCl_3$) ν 2995, 2950, 2920, 2840, 1650, 910, 680 cm^{-1}; MS (CI), m/e 340 (MH^+), MS (EI), m/e (relative intensity) 339 (9), 242 (30), 227 (25), 149 (26), 119 (24), 105 (28), 91 (44), 79 (100), 57 (50).

Acknowledgment. We are grateful to Jean Desmurs, Rhône-Poulenc, Centre de Recherches des Carrières, Saint-Fons for providing the MS spectra.

Relative Reactivities and Stereochemistry for Free-Radical Eliminations of 2-(Aryloxy)-1-phenylpropyl Radicals[1]

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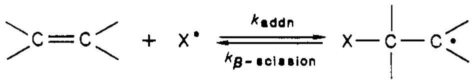
Pacific Northwest Laboratory, Richland, Washington 99352

Received June 8, 1988

The formation of C–C bonds by addition of free radicals to double bonds is gaining wide recognition in the synthesis of organic compounds. The utility of this approach is clearly elucidated by the importance of radical-induced polymerization in chemical industry and, more recently, by the successful application of stereospecific radical addition reactions in the synthesis of natural products.[2,3] The steric and electronic influence of substituents on the rate of addition of free radicals to multiple bonds has been extensively investigated and reviewed.[4]

The unimolecular fragmentation of radical species that occur by scission of the C–heteroatom or C–C bond β to the radical center represents the reverse of radical additions to olefins.



(1)

Numerous examples of C–C bond cleavage of alkoxyl radicals exist in the literature, and in general, the reactions are well understood in terms of steric and polar considerations.[5] Analogous β-scission reactions of carbon-centered radicals have extensive precedent in the high-temperature cracking of paraffins.[6] A representative example is the thermolysis of 1,3-diphenylpropane, which yields an Arrhenius expression of $10^{14.8}\exp(-28\,300/RT)\ s^{-1}$ for the β-scission of benzyl radical from 1,3-diphenyl-1-propyl radical.[7]

Studies of the elimination reactions of β-phenylthiyl, β-phenylsulfinyl, and β-phenylsulfonyl radicals have also been conducted.[8-10] These investigations found no stereoselectivity for the loss of either phenylthiyl or phenylsulfonyl radicals. In contrast, reactions of diastereomeric 2-bromo-3-(phenylsulfinyl)butanes were found to eliminate phenylsulfinyl radicals in a stereoselective manner. This result indicated the rapid loss of phenylsulfinyl radical from the initial nonequilibrium conformations of the radical and was thought to be consistent with the order of leaving-group stability: phenylsulfinyl > phenylsulfonyl ~ phenylthiyl.

Other investigations have addressed the question of substituent effects on the reversible addition of substituted phenylthiyl radicals to olefins.[11,12] These studies concluded that the reaction is goverened by both the thermodynamic stability of $XC_6H_4S^{\bullet}$ and the electronic nature of the olefin, which influences the polar resonance structures in the transition state.

Early studies of the substituent effects on abstraction of hydrogen from phenols by oxygen- and carbon-centered radicals[13-15] revealed excellent correlation with σ^+ parameters and negative ρ value, implying the development of positive charge in the transition state. However, the relative contributions of bond-dissociation energies, resonance effects, and polar transition structures to the observed substituent effects remains controversial.[16,17]

From hydrogen-abstraction studies, we expected the β-scission reactions to exhibit substantial substituent effects. To examine this possibility, and to gain an estimate of the energetics of β-scission, the present study was ini-

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[1] This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC06-76RLO 1830.

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Scheme I. Reaction of 1-Chloro-2-(aryloxy)-1-phenylpropane with Me_3SnH

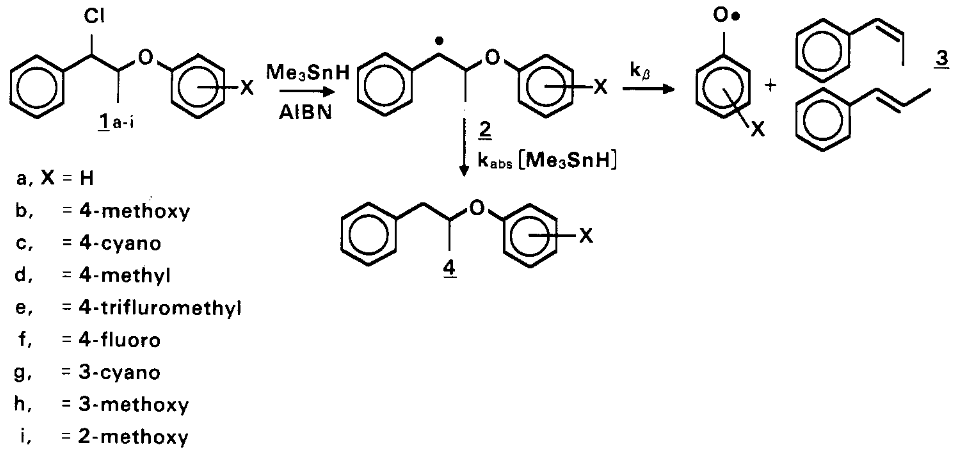

Table I. Relative β-Scission Rates for 2-(Aryloxy)-1-phenylpropyl Radicals at 80 °C

radical	substituent (X)	k_β/k_{abs}	k_β^X/k_β^H
2a	H	0.0218 ± 0.0006	(1)
2b	4-OMe	0.1664 ± 0.0058	4.63
2c	4-CN	0.0239 ± 0.003	1.09
2d	4-CH_3	0.0331 ± 0.006	1.52
2e	4-CF_3	0.0164 ± 0.002	0.75
2f	4-F	0.0468 ± 0.0016	2.15
2g	3-CN	0.0343 ± 0.0004	1.57
2h	3-OMe	0.0217 ± 0.004	0.99
2i[a]	2-OMe	0.611 ± 0.0043	27

[a] The k_β rel value for radical **2i** is excluded from the Hammett plot and the main body of the discussion, due to the likelihood that electronic factors are outweighed by steric effects of the 2-OMe group.

tiated. In addition, the unusually high estimate of the β-scission barrier of the 2-phenoxyl-1-phenylethyl radical[18] (28 kcal mol^{-1}) as well as the reactivity of the β-aryl ether linkages in lignin[19,20] and the possible intermediacy of radical scission pathways during the degradation of lignocellulosic materials[21] piqued our interest.

Results and Discussion

2-(Aryloxy)-1-phenylpropyl radicals **2a–i** were generated from the reaction of the corresponding chlorides **1a–i** with trimethylstannane (Me_3SnH) and azobisisobutyronitrile (AIBN) at 80 °C, Scheme I. In a typical experiment, the reaction was terminated at low conversion (3–5% of the original Me_3SnH concentration) in order to ensure pseudo-first-order conditions in the hydride. The reaction mixture was then assayed by capillary gas chromatography (GC) for the isomeric β-methylstyrenes **3** and the appropriate reduction product **4**.

The ratio **4**/**3** for short extent of hydride consumption is given by eq 2.

$$\frac{[4]}{[3]} = \frac{k_{abs}[Me_3SnH]}{k_\beta} \qquad (2)$$

For each of the chlorides, a minimum of three kinetic runs were carried out at different tin hydride concentrations. Then, in accordance with eq 2, a value for $(k_\beta/k_{abs})^{-1}$ was extrapolated from a plot of [4/3] vs. [Me_3SnH]. Figure 1 shows a representative plot for radical **1d**.

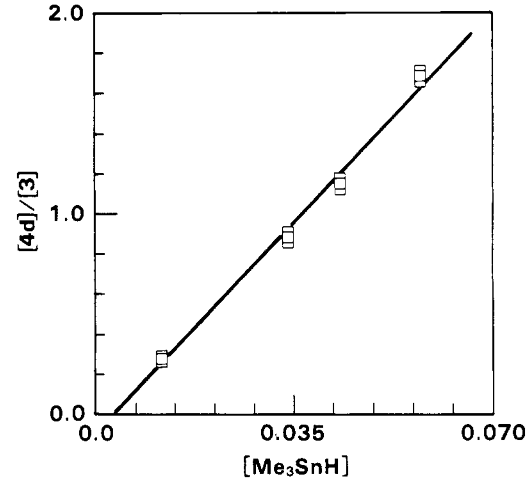

Figure 1. Plot of [**4d**]/[**3**] vs [Me_3SnH] for radical **2d**.

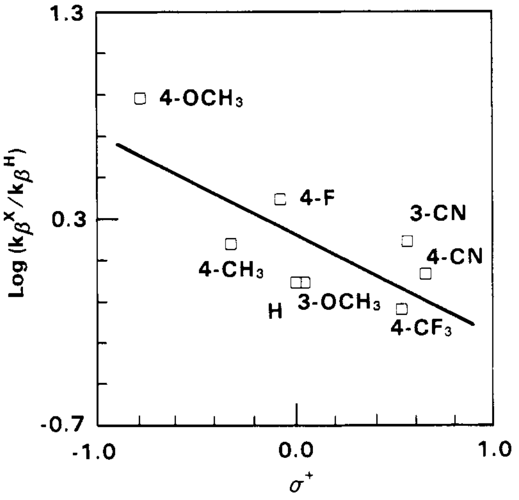

Figure 2. Attempted correlation of σ^+ parameters with log (k_β^X/k_β^H).

Table I lists the relative rate data (k_β/k_{abs}) for the various β-aryloxyl radicals. The influence of substituent on the rate of hydrogen-atom abstraction from the tin hydride by the benzylic radical is assumed to be negligible due to the insulating nature of the C(HMe) group. Thus, the rates for β-scission of aryloxyl radicals can be represented relative to the scission of the parent phenoxyl radical **2a**.

The relative rates of Table I reveal the surprising result that the magnitude of substituent effects is much lower

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for β-scission than for hydrogen-abstraction reactions.[15] Taken with the low activation barrier of 10 ± 2 kcal mol^{-1} estimated for this reaction (vide infra), it is clear that the development of phenoxyl-radical character has occurred in the transition structure, consistent with an early transition state for the β-scission.

In the case of ortho-substituted **2i**, relief of steric congestion in the transition structure is clearly manifested in its much higher rate of β-scission. **2i** was included in this study, but not in the correlation of Figure 2, because the *o*-methoxy isomer is the structural analogue of the β-aryl ether lignin subunit.

It is interesting to compare the range of relative reactivities obtained in the present study, $k_\beta^{4\text{-OMe}}/k_\beta^{\mathrm{H}} = 7.63$, with that previously obtained for β-scission of alkoxyl radicals of the type $R_1R_2R_3CO^\bullet$, where R_1 = Me, R_2 = CH_2Ph, and R_3 = CH_2Ar. The study yielded $k_\beta^{4\text{-OMe}}/k_\beta^{\mathrm{H}}$ = 6.95 at 30 °C,[22] with a σ^+ ρ value of -1.04, which indicates a greater extent of charge development in the transition state for scission of these alkoxyl radicals, even though the scission reaction occurs with a substantially lower activation barrier than that in our ether system.

From previous work in these laboratories[23] and available thermochemical data,[24] the rate constant for hydrogen-atom abstraction from Me_3SnH by the benzylic radicals **2a–i** can be estimated as 1.6×10^4 M^{-1} s^{-1}. Thus, the value of k_β/k_{abs} of 0.019 for radical **2a** translates to an approximate rate constant of 3×10^2 s^{-1} for k_β at 80 °C. Assumption of a typical A factor of $\sim 10^{14}$ for unimolecular scission reactions[24] leads to the value of $E_a \sim 19$ kcal mol for the barrier to β-scission of radical **2a**. This result contrasts with the earlier estimate of 28 kcal mol^{-1} obtained from the thermolysis of phenylethyl phenyl ether.[18] The latter estimate is clearly much too high, in view of data for the elimination of benzyl radicals from 1,3-diphenyl-1-propyl radicals, which also place E_a at $\sim$28.3 kcal mol^{-1}.[7] The enthalpy change ΔH°_{298} for this reaction was calculated as 21.3 kcal mol^{-1}, as compared to an estimate of $\Delta H^\circ_{298} \sim 15.3$ kcal mol^{-1} for the β-scission of radical **2a**. From the much lower enthalpy change for phenoxyl scission, the activation barrier must be lower than the previously published value of 28 kcal mol^{-1}. Work to determine E_a for the β-scission reaction is under way.

Stereochemistry of Elimination. Evaluation of the stereoselectivity for the elimination process required the study of those radicals with the highest observed k_β rel. Thus, *erythro*- and *threo*-2-chloro-1-(2-methoxyphenoxy)propane (**1i**-*erythro*, **1i**-*threo*) were isolated and individually decomposed in the presence of Me_3SnH and AIBN at 80 °C. The reactions were terminated before appreciable olefin isomerization could occur, and the ratios of isomeric styrenes were carefully determined. GC analysis showed the ratios of *trans*- to *cis*-β-methylstyrenes to be roughly equivalent ($\sim$4.5) for both the diastereomeric chlorides. This result clearly indicates that the olefins are formed nonstereospecifically, with the elimination reaction proceeding after equilibration of the rotamers in the intermediate radical.

In conclusion, the relative reactivities for scission of 2-(aryloxy)-1-phenylpropyl radicals reported here provide the first opportunity for evaluation of the steric and electronic factors that control this reaction. Our results show negligible correlation of the k_β rel data with σ^+ substituent parameters, a finding consistent with an early transition state exhibiting little charge development, in great contrast to substituent effects in hydrogen abstraction from phenols.[15] Finally, there is no stereoselectivity in the elimination of the aryloxyl radical. An estimate for the barrier to β-scission of 2-phenoxy-1-phenylpropyl radical places E_a at $\sim$19 kcal mol^{-1}. Studies are under way to establish an absolute rate expression and the Arrhenius parameters for this process. An AM1 semiempirical study has also been initiated to determine the geometry, stereochemistry, and charge separation in the transition state for the β-scission reaction.

Experimental Section

General. ^{1}H NMR spectra were determined with a Varian VXR-300 spectrometer. Gas chromatography was carried out on a Hewlett-Packard Model 5880A instrument equipped with an on-column injector and flame-ionization detection. Analyses were performed on 20-m J & W Scientific DB-1 and DB-5 capillary columns. GC–mass spectrometry was carried out with a Hewlett-Packard 5985 system.

Reagents. Reagent grade benzene and *trans*-β-methylstyrene were purchased from the Aldrich Chemical Co. and used as received. AIBN was obtained from Aldrich, recrystallized twice from methanol, and stored at -30 °C. Trimethylstannane (Me_3SnH) was prepared from trimethyltin chloride (Aldrich) and lithium aluminum hydride by the procedure of Kuivila.[25] Quantitative assays of this reagent by complete consumption in the presence of a standard halide showed >99% purity. The Me_3SnH was handled under ultrapure nitrogen at all times and was stored at -30 °C.

Chlorides 1a–i were prepared from the corresponding alcohols, for which a general procedure exists in the literature.[26] Chlorination was effected by treatment with thionyl chloride in benzene at ambient temperature, followed by column chromatography (200-mesh silica with dichloromethane as eluent). With the exception of **1a**, which was isolated as the pure erythro and threo forms, all chlorides were obtained as diastereomeric mixtures and used as such.

Reduction products 4a–i were required as GC standards, and all were independently synthesized according to the following general procedure: 250 mg of the chloride, 25 mg of AIBN, and 1.1 equiv of triphenylstannane (Alpha Chemical Co.) in 20 mL of benzene were refluxed under nitrogen until GC analysis showed complete conversion of the chloride. After removal of solvent, the mixture was distilled with a Kugelrohr apparatus (0.025 Torr) to effect separation of the nonvolatile tin residues, followed by column chromatography (200-mesh silica with dichloromethane as eluent). In all cases, thorough NMR characterization was carried out to confirm the structures.

Kinetic Experiments. In a typical experiment, 20 mg of the chloride, 5 mg of AIBN, 300 μL of a 2×10^{-2} M solution of isobutylbenzene in benzene (internal standard), and 75 mg of Me_3SnH were added to a volumetric flask and brought to the 10-mL volume mark with degassed benzene. Pyrex tubes purged with nitrogen were each charged with 0.5-mL aliquots of the stock solution and sealed under vacuum after three freeze–pump–thaw cycles (the tubes were back-filled with nitrogen before each thaw cycle to prevent escape of the volatile Me_3SnH). The samples were heated in a Braun Thermomix 1480 oil bath equilibrated at 80.0 ± 0.1 °C. After an appropriate thermolysis time, typically between 5 and 20 min, the reaction was quenched by immersion of the tubes in ice water. The ampules were stored in liquid nitrogen prior to analysis by GC.

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Registry No. **1a**, 117860-73-8; **1b**, 117860-74-9; **1c**, 117860-75-0; **1d**, 117860-76-1; **1e**, 117860-77-2; **1f**, 117860-78-3; **1g**, 117860-79-4; **1h**, 117860-80-7; **1i**, 117860-81-8; **2a**, 117860-82-9; **2b**, 117860-83-0; **2c**, 117860-84-1; **2d**, 117860-85-2; **2e**, 117860-86-3; **2f**, 117860-87-4; **2g**, 117860-88-5; **2h**, 117860-89-6; **2i**, 117860-90-9; Me_3SnH, 1631-73-8.

Photochemistry of Bichromophoric Aromatic Diketones: The Effect of Methylene Chain

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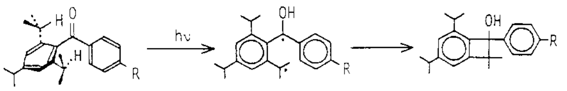
Reaction mechanism for photocyclization of 2,4,6-triisopropylbenzophenone (TIBP, **3**) into its benzocyclobutenol has been studied in great detail (eq 1).[1-3] Subsequent studies on bichromophoric *m*-acyl-substituted TIBP such as **5** have revealed[4] that two constituent carbonyl groups in the molecule are relatively independent because of their cross-conjugation, e.g., the absorption spectrum of **5** is approximately equal to the sum of the absorption spectra of benzophenone BP (**1**) and TIBP. Furthermore, it has been deduced from quenching experiments of the reaction that the triplet excitation is rapidly equilibrated between the two carbonyl groups in the molecule, with the equilibrium highly shifted toward the hindered carbonyl group ($k_{et} \gg k_{-et}$ in eq 2). The preferential energy transfer toward the hindered carbonyl group was explained on the basis of entropy considerations.[4]



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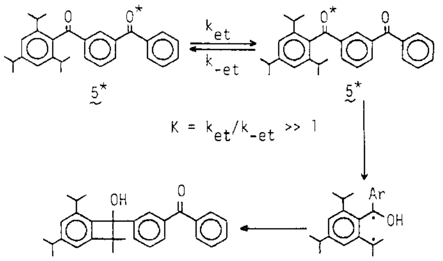
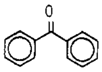


(2)

It has recently been reported that, for conjugated polyenes or polyynes bearing a suitable chromophore at each end, very efficient energy transfer or charge transfer is possible through the conjugated linker.[5] Considering the potential utility of these conjugated molecules as novel molecular electronic devices for memory and switching, we are interested in the mechanism of the totally efficient intramolecular energy migration in diketone **5**. In this connection, we now studied the photochemistry of bichromophoric aromatic diketones **6a–c**, where the two chromophores are separated by one to three methylene groups. Phosphorescence and photocyclization quantum yield studies suggest that the efficiency for intramolecular energy transfer is **6c** > **6b** ≳ **6a**.



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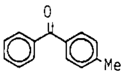

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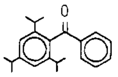
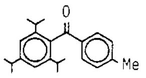


3,TIBP



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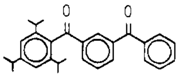
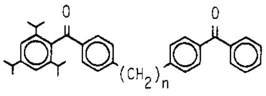
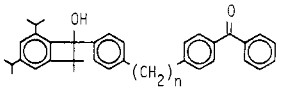


5



6a - c



7a - c

a, n = 1; b, n = 2; c, n = 3

Results

Spectroscopic Study. Phosphorescence spectra of diketones **6a–c** were measured in rigid glasses at 77 K ([**6**] ~ 10^{-3} M). Their shapes and positions of emission maxima were very similar to those of BP. Triplet energies (E_T) estimated from the phosphorescence 0–0 band, the relative phosphorescence intensities, and the absorption maxima of π,π^* and n,π^* bands for **6a–c** are summarized in Table I. The data for reference compounds **1–5** are also listed in the same table for comparison.

Preparative Photolyses. Irradiations of diketones **6a–c** in benzene solutions (0.01–0.05 M) with the Pyrex-filtered light for 10 h produced the corresponding benzocyclobutenols **7a–c**. The products were isolated by column chromatography on silica gel. Product balance was excellent in each case (isolation yield: 90% for **7a**, 84% for **7b**, 80% for **7c**).

Quantum Yields. Degassed benzene solutions of **6a–c** (0.001–0.05 M) were irradiated on a merry-go-round apparatus with the potassium chromate filtered light (mainly 313 nm) at 25 °C. The products **7a–c** were analyzed by HPLC, and their quantum yields Φ_{CB} were calculated with reference to the photocyclization of **3** ($\Phi_{CB} = 0.60$ at 0.1 M[1]). The results are summarized in Table II.

Discussion

The n,π^* and π,π^* absorption spectra of diketones **6a–c** (Table I) are approximately equal in both wavelength and absorption coefficient to the combined spectrum of 4-methylbenzophenone (**2**) and 4-methyl-2′,4′,6′-triisopropylbenzophenone (**4**). Thus, any ground-state intramolecular electronic interactions between the two benzophenone chromophores are not detectable from the absorption spectra of **6a–c**.

The phosphorescence intensities for **6a** and **6b** in ethanol glass or methylcyclohexane (MC) glass at 77 K are moderate: their relative intensities are 0.2–0.4 as compared with that of BP (1.0) (Table I). The phosphorescence intensity for **6c** is also moderate in ethanol glass (the relative intensity, 0.32). In MC glass, in contrast, **6c** is weakly phosphorescent, and its intensity (0.053) is as low as that of TIBP (0.039). The low quantum yield of emission for TIBP is ascribable to intramolecular hydrogen abstraction.[1-3] The moderate but reduced phosphorescence efficiency for **6a** and **6b** (and **6c** in ethanol) as compared with BP is not surprising, because some of the light is absorbed directly by the isopropyl-substituted benzophenone chromophore.

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