

solvents. However, the properties which are usually considered as characteristic of the hydrophobic effect (i.e., low solubility of nonpolar molecules and association of nonpolar species in water) are unrelated to the unique fluctuational situation in water.

As mentioned above, the studies in EAN suggest that the fluctuation behavior is not a prerequisite for micellization at least as far as cmc's are concerned. Recent work of Evans and Wightman on micelle formations above 100 °C in water provides further supporting evidence.⁶⁹ Cmc's determined for tetradecyltrimethylammonium bromide in water from 25 to 166 °C increased only 10-fold over this temperature range. The peculiar behavior of water, however, gradually disappears as the temperature is increased, and water begins to behave more like a regular liquid. Hence, the interesting question of how the restructuring of water around the hydrocarbon chains influences the cmc's as well as their aggregation numbers remains open.

Conclusion

In view of the crucial role of water to terrestrial processes, especially biological ones, it is of great importance to separate those of its properties which are essential to hydrophobic inter-

(69) Evans, D. F.; Wightman, P. J. *J. Colloid Interface Sci.* **1982**, *86*, 515-24.

actions from those which are correlated, but largely irrelevant. The Benzinger-Frank-Lumry analysis preserves most of the Frank-Evans picture of water structure but removes the emphasis on entropies and heat capacities of solution as factors of commanding importance to the hydrophobic behavior of water as a solvent. The recent studies of Evans and his associates and the results presented here are the first tests of this change in viewpoint and strongly confirm it through thermodynamic properties for solution of nonpolar gases in EAN, and through its ability to produce micelles from surfactants. Its failure to demonstrate water-like heat capacity behavior serves to differentiate those properties of water which are due to fluctuations between different isomeric states, from those which are caused by its high cohesive energy.

Acknowledgment. This work was supported by NSF Grant CHE-8006202 to E.M.A. We appreciate the help of Mr. Andrew Maynard supported by the NSF Undergraduate Research Program. We are much indebted to Professors D. F. Evans, R. Lumry, and H. S. Frank for sharing viewpoints and results prior to publication.

Registry No. H₂O, 7732-18-5; methanol, 67-56-1; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; DMSO, 67-68-5; DMF, 68-12-2; NMF, 123-39-7; ethylene glycol, 107-21-1; EAN, 22113-86-6; urea, 57-13-6.

Novel Photoreversible Cyclization of Acyl-Substituted 2,4,6-Triisopropylbenzophenones¹

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Abstract: A photoreversible cyclization of 3'(or 4')-X-2,4,6-triisopropylbenzophenones **1** (X = C₆H₅CO, 2,4,6-(i-Pr)₃C₆H₂CO, CH₃CO) into the corresponding **2** was investigated in benzene at 313 nm. When the meta (2,4,6-(i-Pr)₃C₆H₂CO) derivative **1d** was photolyzed, an additional product, 1,1'-(*m*-phenylene)bis(benzocyclobutenol) (**3d**), arising from further photocyclization was also obtained. On the contrary, the para (2,4,6-(i-Pr)₃C₆H₂CO) derivative **1c** did not further photocyclize. Diene-quenching experiments of the back-photoreaction **2** → **1** revealed that cleavage of the C₁-C₂ single bond in the benzocyclobutenol ring occurred much faster with para (4'-X) substituents (>10¹⁰ s⁻¹) than with meta (3'-X) substituents (~10⁸ s⁻¹). These results were explained by the difference in spin densities at the para and meta positions. The reaction **2** → **1**, where X is benzoyl group, can be categorized into a novel π*-orbital-initiated photoreaction of simple substituted benzophenones.

Introduction

The excited states of simple aromatic ketones are characterized by extremely rapid and quantitative intersystem crossing ($k_{ST} > 10^{10} \text{ s}^{-1}$, $\phi_{ST} = 1.0$).² Hence, benzophenone and acetophenone are frequently used as typical triplet sensitizers completely free from complications due to singlet sensitization. The photoreactions of these ketones, e.g., hydrogen abstraction,² oxetane formation,² α -cleavage,² and others,³ are usually interpreted in terms of singly occupied n-orbital initiation, explicitly considering in certain cases a bimolecular interaction of charge-transfer nature which occurs

Table I. Products and Isolation Yields from Photolyses of Acyl-Substituted 2,4,6-Triisopropylbenzophenones **1a-f** in Benzene

starting material	irradiation time, h	photolyses products (isolation yields, %)
1a	3	2a (24), 1a (73)
1b	3	2b (63), 1b (30)
1c	7	2c (23), 1c (74)
1d	0.7	2d (25), 3d (60), 1d (7.5)
1e	2.5	2e (62), 1e (31)
1f	3	2f (73), 1f (13)

prior to actual bond formation (or rupture).⁴ Indeed, π*-orbital-initiated photoreactions of simple substituted benzophenones with T₁(n,π*) states appear so far to be unknown.⁵

(4) For example, photoreduction by amines (Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141) and by phenols (Das, P. K.; Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4154).

(1) Photoinduced reactions, part 141.

(2) See any standard textbook on photochemistry: for example, Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978.

(3) For example: (a) Barwise, A. J. G.; Gorman, A. A.; Leyland, R. L.; Parekh, C. T.; Smith, P. G. *Tetrahedron* **1980**, *36*, 397. (b) Fox, M. A. *J. Am. Chem. Soc.* **1979**, *101*, 5339. (c) Nowada, K.; Hisaoka, M.; Sakuragi, H.; Tokumaru, K.; Yoshida, M. *Tetrahedron Lett.* **1978**, 137. (d) Davis, D. D.; Ahmed, F. U. *J. Am. Chem. Soc.* **1981**, *103*, 7653.

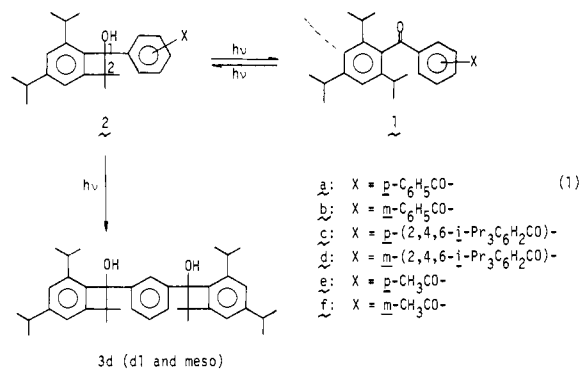
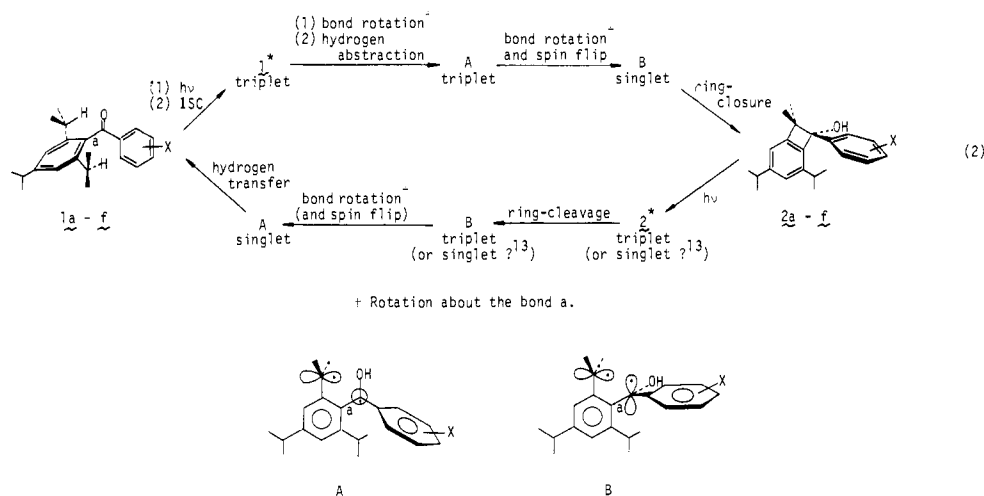


Table II. Quantum Yields for Photocyclization (1 → 2) and Photoreketonization (2 → 1)

compd	$\phi(1 \rightarrow 2)^a$	$\phi(2 \rightarrow 1)^a$
a	0.16	0.34
b	0.64	0.38
c	0.10	0.40
d	0.79	0.38 ^b
e	0.06	0.33
f	0.25	0.36

^a Determined in degassed benzene at 25 °C, using potassium chromate filtered light (313 nm); concentrations in 1 or 2 = 0.05 M. Reaction 1 (X = H) → 2 (X = H) was used as an actinometer ($\phi = 0.60$).^{9a} ^b $\phi(2d \rightarrow 3d) = 0.34$.



As an extension of our study on the energy-storing photochemistry of 2,4,6-triisopropylbenzophenone (**1**, X = H),⁹ we are studying photolyses of its homologues, e.g., **1a-f**. Here we report an intramolecular photocleavage of a cyclobutenol ring, a rapid process formally initiated by a singly occupied π^* (or π) orbital of the aromatic ketone moiety in a molecule, and a novel spin density effect.

Results and Discussion

Irradiations of solutions (10^{-2} M) of para- and meta-acyl-substituted 2,4,6-triisopropylbenzophenones **1a-f** in benzene through Pyrex under bubbling nitrogen produced the corresponding benzocyclobutenols **2a-f**. In the case of **1d** a further photocyclization proceeded to give 1,1'-(*m*-phenylene)bis(benzocyclobutenol) (**3d**) as a mixture of *dl* and *meso* isomers. These products were isolated by column chromatography on silica gel. Product balance was excellent in each case as shown in Table I.

The reaction **1** → **2** was found to be photoreversible, and irradiation of either **1** or **2** for a few hours (2–3 h) resulted in a

photostationary mixture of **1** and **2** except in the case of **1d** (or **2d**), where a prolonged irradiation (4 h) afforded only **3d**.

Table II summarizes the quantum yields for benzocyclobutenol formation (**1** → **2**, and **2d** → **3d**) and back-photoreaction (**2** → **1**), which were determined in a degassed benzene solution (0.05 M) at very low conversions (<1%) by irradiation at 313 nm, using for product analyses high-pressure liquid chromatography (HPLC). The photocleavage reaction **2** → **1** proceeded with nearly the same efficiency ($\phi = 0.33$ –0.40) for a variety of substituents, while the efficiency of cyclobutenol formation varied considerably with substitution ($\phi = 0.06$ –0.79).

In analogy to the mechanism for photocyclization of **1** (X = H) into **2** (X = H) where the importance of bond rotation around bond a was stressed,^{9a,f} the interconversions **1a-f** ⇌ **2a-f** probably proceeded along the diradical pathway shown in eq 2. A and B are different conformations of the same diradical species. Since the 2,4,6-triisopropylbenzoyl group is severely twisted in the most strain-free conformation of molecule **1**,^{9a,f} rotation around bond a will be required before occurrence of intramolecular hydrogen abstraction by the carbonyl group in the n,π^* triplet state. In fact, the triplet lifetime of **1** (X = H) (90 ns) was shown to be controlled by hindered rotation around bond a.^{9a,f}

Table II shows that the sum of quantum yields for the transformation **1d** ⇌ **2d** exceeds 1.0 ($\phi(1d \rightarrow 2d) + \phi(2d \rightarrow 1d) = 1.17$), even though one-third of excited **2d** gives **3d** ($\phi(2d \rightarrow 3d) = 0.34$). It seems that the sum of quantum yields for **1b** ⇌ **2b** also exceeds 1.0. These results support the fact that transformations **1d** → **2d** (or **1b** → **2b**) and **2d** → **1d** (or **2b** → **1b**) proceed along two kinetically distinct routes via the same diradical intermediate as illustrated in eq 2. However, since a full discussion of the detailed mechanism for interconversion **1** ⇌ **2**, where X = OMe, Me, H, CO₂Me, CF₃, and CN, has already been reported,^{9a-f} further discussion will not be attempted here.

It is noticeable in Table II that, in contrast with the competitive transformation of **2d** into **1d** and **3d** ($\phi = 0.38$ and 0.34, respectively), the corresponding para isomer **2c** gave only **1c**. This result suggests that the rate for bond cleavage of the cyclobutenol

(5) For acetophenone and related compounds, examples of (presumably) π^* - (or π -) orbital-initiated photoreactions are known, e.g., β -cleavage,⁶ dienone rearrangement,^{7a} di- π -methane rearrangement,^{7b,c} and aromatic substitution.^{7d} Also consider the photorearrangement of anthrone derivatives.⁸

(6) (a) Loutfy, R. O.; Yates, P. *J. Am. Chem. Soc.* **1979**, *101*, 4694. (b) Hallet, P.; Muzart, J.; Pete, J. *J. Org. Chem.* **1981**, *46*, 4275.

(7) (a) Smith, A. B.; Agosta, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 1961. (b) Demuth, M.; Amrein, W.; Bender, C. D.; Braslavsky, S. E.; Burger, U.; George, M. V.; Lemmer, D.; Schaffner, K. *Tetrahedron* **1981**, *37*, 3245. (c) Van der Weerd, A. J. A.; Cerfontain, H. *Ibid.* **1981**, *37*, 2121. (d) Colb, A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3416.

(8) Montet, J.-C.; Reverdy, G. *Bull. Soc. Chim. Fr.* **1978**, II, 442.

(9) (a) Ito, Y.; Umehara, Y.; Hijiya, T.; Yamada, Y.; Matsuura, T. *J. Am. Chem. Soc.* **1980**, *102*, 5917. (b) Ito, Y.; Umehara, Y.; Yamada, Y.; Matsuura, T. *J. Chem. Soc., Chem. Commun.* **1980**, 1160. (c) Hayashi, H.; Nagakura, S.; Ito, Y.; Umehara, Y.; Matsuura, T. *Chem. Lett.* **1980**, 939. (d) Ito, Y.; Umehara, Y.; Yamada, Y.; Matsuura, T.; Imashiro, F. *J. Org. Chem.* **1981**, *46*, 4359. (e) Ito, Y.; Nishimura, H.; Matsuura, T. *J. Chem. Soc., Chem. Commun.* **1981**, 1187. (f) Ito, Y., et al., manuscripts submitted for publication.

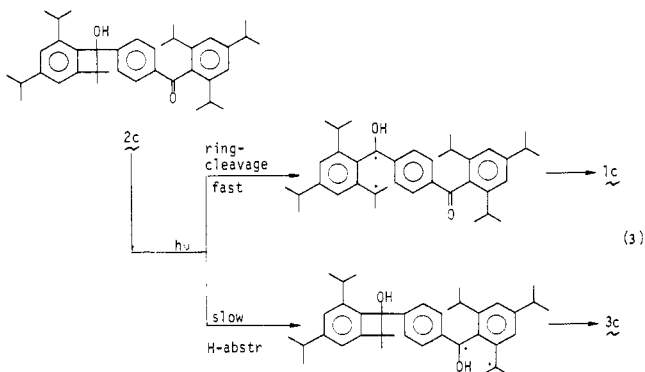
Table III. Absorption Spectra of 2a-f and Related Compounds in Nonpolar Solvents^a

compound	λ_{\max} , nm (e)	
	n, π^*	π, π^*
2a	348 (180)	261 (24 300)
2b	345 (140)	248 (20 000)
2c	348 (85)	259 (21 300)
2d	346 (78)	249 (13 000)
1 (X = H)	349 (63)	242 (15 700)
2 (X = H)	none	267 (14 00)
benzophenone (B)	346 (120) ^b	248 (19 400) ^b
p-methyl-B	345 (160) ^b	252 (18 800) ^b
m-methyl-B	345 (110) ^b	250 (18 000) ^b
2e	328 sh (82)	253 (23 000)
2f	328 sh (50)	242 (12 700)
acetophenone (A)	320 (41) ^c	237 (12 500) ^d
p-methyl-A	318 (54) ^c	247 (15 000) ^d
m-methyl-A		241 (11 300) ^d

^a In cyclohexane, unless otherwise specified; sh, shoulder.

^b Rekker, R. F.; Nauta, W. T. *Recl. Trav. Chim. Pays-Bas* 1961, 80, 747 (in isooctane). ^c Tanaka, J.; Nagakura, S.; Kobayashi, M. *J. Chem. Phys.* 1956, 24, 311 (in *n*-heptane). ^d Forbes, W. F.; Mueller, W. A.; Ralph, A. S.; Templeton, J. F. *Can. J. Chem.* 1957, 35, 1049.

ring in 2c is much faster than the rate of intramolecular hydrogen abstraction by the n, π^* carbonyl (eq 3). We have previously



found that 1 (X = H) in its $T_1(n, \pi^*)$ state undergoes intramolecular hydrogen abstraction with a rate $\sim 10^7$ s⁻¹.^{9a,f} It may also be noted that values of $\phi(1 \rightarrow 2)$ for the meta-acyl-substituted compounds 1b and 1d ($\phi = 0.64$ and 0.79, respectively) are slightly higher than $\phi(1 \rightarrow 2)$ of the unsubstituted compound 1 (X = H) ($\phi = 0.60$). The opposite effect of acyl substitution was recently reported by Wagner on the type II reaction of valerophenone.¹⁰

The ring-opening reaction 2 \rightarrow 1 is an unusual reaction in that a cyclobutenol ring undergoing rupture is separated from the carbonyl group in the molecule. The photochemistry of bichromophoric molecules such as 2 is of current interest.¹¹ Table III shows that the absorption spectra of 2a-f are similar to those of the benzophenones or acetophenones of related structures. Closer examination of the table, however, indicates that some weak electronic interactions between the two separated π systems in a molecule might be present, especially in the case of the para-acyl-substituted compounds 2a, 2c, and 2e. Phosphorescence spectra in ethanol glass of 2a, 2b, and benzophenone were indistinguishable both in band shape and in wavelength at maximum emission. However, their intensities were considerably different: (relative intensity) 2a:2b:benzophenone = 0.032:0.38:1.0. Energy dissipation through the facile ring cleavage is probably responsible for the weak phosphorescence of 2a and 2b.

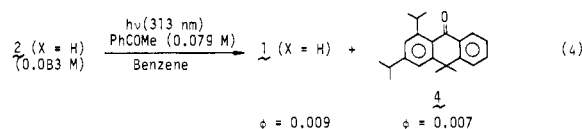
The reaction 2 \rightarrow 1 seems to be a result of an unusual intramolecular energy transfer from the carbonyl chromophore to the benzocyclobutenol moiety, since the acetophenone or benzophenone

Table IV. Quenching Constants ($k_q\tau$) and Triplet Lifetimes (τ) for Benzocyclobutenols 2a-f in Degassed Benzene at 313 nm

compd	$k_q\tau$, M ⁻¹ a,b	$1/\tau$, $\times 10^8$ s ⁻¹ c
2a	<0.5	>100
2b	29	1.7
2c	<0.5	>100
2d	21, 190 ^d	2.4, 0.26 ^d
2e	<0.5	>100
2f	9.4	5.3

^a From diene quenching of the formation of 1, unless otherwise specified. ^b Maximum error 20%. ^c Based on $k_q = 5 \times 10^9$ M⁻¹ s⁻¹ in benzene. ^d From diene quenching of the formation of 3d. Both meso and dl isomers of 3d gave the same result within experimental error.

triplet sensitized very inefficiently the cleavage of 2 (X = H) into 1 (X = H) as shown in eq 4.¹² In this case the substituted



anthrone 4 was also formed with nearly the same efficiency as that of 1 (X = H). It was found that the addition of 0.083 M 2 (X = H) to the solution of acetophenone (0.079 M) in benzene led to as much as a 30% decrease in the acetophenone phosphorescence intensity at room temperature, indicating that 30% of the acetophenone triplet was quenched by 2 (X = H) (probably hydrogen abstraction is a main quenching mechanism) under the reaction conditions described in eq 4. Thus it seems that the reaction 2a-f \rightarrow 1a-f was initiated by some direct intramolecular electronic interaction between the excited ketone moiety and the cyclobutenol ring.

Table IV summarizes the triplet quenching data for the photocleavage reaction 2 \rightarrow 1, using piperlyene and/or 2,5-dimethyl-2,4-hexadiene (0-0.2 M) as triplet quencher. The effect of diene on the para-substituted compounds 2a, 2c, and 2e was undetectable in each case ($k_q\tau < 0.5$ M⁻¹). On the other hand, the effect was observable for the meta-substituted compounds 2b, 2d, and 2f ($k_q\tau = 29, 21,$ and 9.4 M⁻¹, respectively), indicating that the rate of bond cleavage of the cyclobutenol ring ($1/\tau$) is much slower in the meta-substituted cases ($\sim 10^8$ s⁻¹) than in the para-substituted cases ($> 1 \times 10^{10}$ s⁻¹).¹³ It should be noted that the magnitude of this rate seems independent of the nature (n, π^* or π, π^*) of T_1 states. Ketones 2a-d are expected to have $T_1(n, \pi^*)$ states,^{9a} and 2e and 2f $T_1(\pi, \pi^*)$ states with $T_2(n, \pi^*)$ states lying slightly higher.¹⁶

Table IV shows that photocyclization of 2d into 3d was also quenchable by diene, and its quenching efficiency ($k_q\tau = 190$ M⁻¹) was definitely different from that for the photocleavage 2d \rightarrow 1d ($k_q\tau = 21$ M⁻¹). This result is not unusual when we consider the following difference in the reaction mechanism: as aforementioned, the transformation of 2d triplet into 3d requires a hindered bond rotation in the 2,4,6-triisopropylbenzoyl group prior to occurrence of the benzylic hydrogen abstraction, whereas the decay of 2d triplet via the cyclobutenol ring cleavage does not require this bond rotation. The observation of two kinetically distinct

(12) The reaction was stopped at a very low conversion ($\sim 0.005\%$) to suppress the undesirable effects of 1 (X = H) and 4 produced. The benzophenone sensitization gave a similar result.

(13) In the case of the para compounds 2a, 2c, and 2e, the $S_1(n, \pi^*)$ states may be involved in the photocleavage 2 \rightarrow 1. The reaction due to benzophenone singlet may occur under certain conditions.¹⁴ Singlet-state reactions of acetophenone derivatives are known.¹⁵

(14) Schilling, M. L. M. *J. Am. Chem. Soc.* 1981, 103, 3077.

(15) (a) Gonzenback, J.-U.; Schaffner, K.; Blank, B.; Fischer, H. *Helv. Chim. Acta*, 1973, 56, 1741. (b) Fonassier, J. P.; Merlin, A. *J. Photochem.* 1980, 12, 17. (c) Wagner, P. J.; Chen, C.-P. *J. Am. Chem. Soc.* 1976, 98, 239.

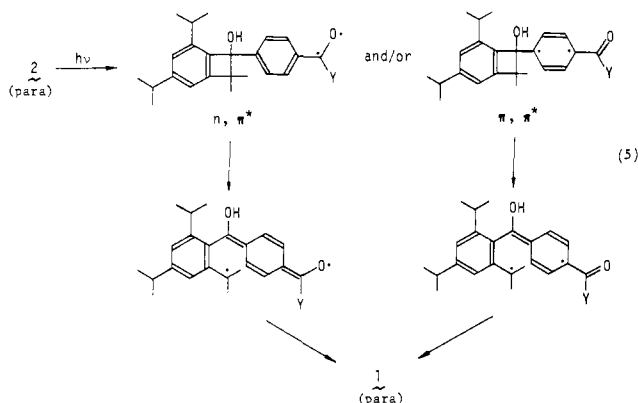
(16) Wagner, P. J.; Thomas, M. J.; Harris, E. J. *J. Am. Chem. Soc.* 1976, 98, 7675.

(10) Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.* 1981, 103, 7329.

(11) (a) Morrison, H. *Acc. Chem. Res.* 1979, 11, 383. (b) Schryver, F. C.; Boens, N.; Put, J. *Adv. Photochem.* 1977, 10, 359.

triplets as a result of slow conformational mobility of molecules is common.¹⁷

However, whatever the multiplicity (S or T) and the nature (n, π^* or π, π^*) of the responsible states for the photocleavage $2 \rightarrow 1$ are, this type of photoreaction is novel for simple aromatic ketones in that the reaction was formally initiated by the singly occupied π^* (or π) orbital (cf. eq 5). In this connection, it is



very interesting to note the fact that the aromatic ketones in their n, π^* or π, π^* triplet states have much higher spin densities at the para position than at the meta position.¹⁸ As is illustrated in eq 5 in terms of one of the common valence-bond structures for the n, π^* and π, π^* triplets,^{18b} this difference in spin density nicely explains the much faster ring-opening rate of the para-substituted compounds (**2a**, **2c**, and **2e**), compared with that of the meta-substituted ones (**2b**, **2d**, and **2f**) (Table IV). Evidently as a result of this very rapid ring cleavage for the para cases, **2c** gave selectively **1c** without further photocyclization into **3c**. A similar big difference in the intramolecular CT quenching rate between para- and meta-substituted valerophenone derivatives^{18a} may also be ascribed (at least partly) to the spin-density difference.

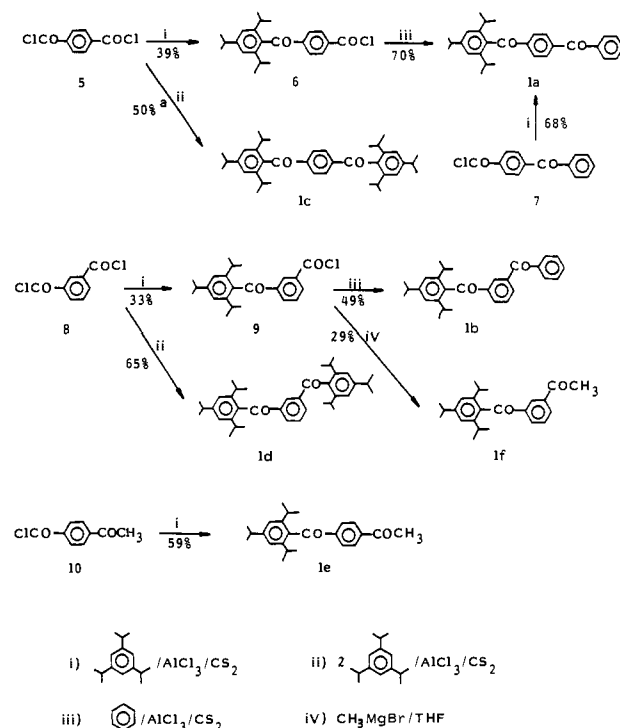
Experimental Section

All melting points are uncorrected. The NMR, IR, UV, and emission spectra were measured by Varian T-60 (or Varian HA-100), JASCO IRA-1, Shimadzu UV-200, and Shimadzu RF-500 spectrometers, respectively. Thin layer chromatography was done on a Merck TLC plastic sheet precoated with silica gel 60 F₂₅₄ (for analytical purposes) or on a Merck Kieselgel 60 PF₂₅₄ (for preparative purposes). Column chromatography was carried out on silica gel (Wakogel C-200). HPLC analyses were performed with a JASCO Twinkle chromatograph equipped with a UVIDE-100 UV detector, using silica gel column (SS-05) and hexane/ethyl acetate eluent.

Preparation of Para- and Meta-Acyl-Substituted 2,4,6-Triisopropylbenzophenones. Compounds **1a-f** were prepared as shown in Chart I by the usual Friedel-Crafts reactions. Typical procedures for the synthesis of **1b**, **1d**, and **1f** are as follows.

To a well-stirred solution containing 50 g (246 mmol) of isophthaloyl chloride (**8**) and 44 g (331 mmol) of AlCl₃ in CS₂ (700 mL) was added dropwise 50 g (245 mmol) of 1,3,5-triisopropylbenzene in CS₂ (300 mL) over a period of 5 h at room temperature. Stirring was continued for an additional 50 h. The reaction mixture was poured over ice-water containing 200 mL of HCl aqueous solution (30%). The CS₂ layer was separated and washed with a saturated solution of NaHCO₃ and then with water. The aqueous layer was extracted with ether, and the ethereal layer was washed similarly. The combined organic layer was dried over MgSO₄ and evaporated under reduced pressure. The residue containing **1d** as a byproduct was fractionally crystallized from hexane to afford 30 g (33% yield) of *m*-(2,4,6-triisopropylbenzoyl)benzoyl chloride (**9**): mp 127–128 °C; IR (Nujol) 1785 (COCl), 1745 (COCl), 1685 (C=O) cm⁻¹; NMR (CDCl₃) δ 8.67 (1 H, br s, arom), 8.40–8.00 (2 H, m, arom),

Chart I



^aReference 19.

7.76–7.43 (1 H, m, arom), 7.10 (2 H, s, arom), 3.23–2.27 (3 H, m, (CH₃)₂CH), 1.25 (6 H, d, *J* = 7 Hz, *p*-(CH₃)₂CH), 1.10 (12 H, d, *J* = 7 Hz, *o*-(CH₃)₂CH).

A solution containing 15 g (41 mmol) of **9** and 12 g (90 mmol) of AlCl₃ in CS₂ (75 mL) was mixed with 75 mL (841 mmol) of benzene and the mixture was stirred at room temperature for 2 h. After similar workup the residue was crystallized from methanol to give 8 g (49% yield) of 1-benzoyl-3-(2,4,6-triisopropylbenzoyl)benzene (**1b**).

In a similar manner 1,3-bis(2,4,6-triisopropylbenzoyl)benzene (**1d**) was synthesized from 25 g (123 mmol) of **8**, 54.7 g (268 mmol) of 1,3,5-triisopropylbenzene, and 76 g (570 mmol) of AlCl₃ in 65% yield.

A solution of methylmagnesium bromide (2.4 g, 20 mmol) in THF (20 mL) was added dropwise to a solution of **9** (7.4 g, 20 mmol) in dry THF (15 mL) over a period of 30 min. The temperature was maintained at -78 °C during the course of the addition. Then the mixture was brought to room temperature and stirred for 1 h at this temperature. The solution became clear during this time. After addition of 150 mL of water the reaction mixture was extracted with ether. The ethereal layer was washed with 1 N NaOH solution, then with water, and dried over MgSO₄. After evaporation of the solvent, separation was done by column chromatography on silica gel using petroleum ether and benzene as eluent. Along with 1.0 g of a byproduct (probably a benzil derivative,²⁰ mp 187–188 °C; IR (Nujol) 1710 (C=O), 1690 cm⁻¹ (C=O)), 2.0 g (29% yield) of 1-acetyl-3-(2,4,6-triisopropylbenzoyl)benzene (**1f**) was obtained.

Melting points, recrystallization solvents, IR, NMR, and microanalytical data for **1a-f** are summarized in Tables V and VI.

Preparative Photolyses. All irradiations were carried out with a 400-W high-pressure mercury lamp through Pyrex under bubbling nitrogen; the products were separated by chromatographic methods. A typical procedure for **1d** is as follows.

A solution of **1d** (2.00 g) in benzene (500 mL) was irradiated for 40 min. After evaporation of the solvent under reduced pressure, the residue was subjected to column chromatography on silica gel (60 g). Elution with 600 mL of petroleum ether-benzene (7:3 v/v) gave 150 mg (7.5% yield) of recovered **1d**. Further elution with 800 mL of benzene afforded 500 mg (25% yield) of 4,6-diisopropyl-2,2-dimethyl-1-[*m*-(2,4,5-triisopropylbenzoyl)phenyl]-1,2-dihydrobenzocyclobuten-1-ol (**2d**). Further elution with 300 mL of benzene gave a small amount of additional **2d**. Further elution with 900 mL of benzene yielded 640 mg (32% yield) of one stereoisomer (a higher melting isomer) of 1,1'-(*m*-phenylene)bis-(4,6-diisopropyl-2,2-dimethyl-1,2-dihydrobenzocyclobuten-1-ol) (**3d**). Further elution with 700 mL of benzene-CHCl₃ (4:1 v/v) gave 560 mg

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Table V. Properties of Acyl-Substituted 2,4,6-Trisopropylbenzophenones and the Corresponding Benzocyclobutenols

compd	mp, °C	recrystn solvent	IR (Nujol), cm ⁻¹ (C=O and/or OH)	NMR (CDCl ₃), δ			
				arom	isopropyl methine ^c	methyl	OH
1a	168–169.5	C ₆ H ₆ -EtOH	1670	8.00–7.36 (9 H, m), 7.03 (2 H, s)	2.92 (1 H, sep, <i>J</i> = 7 Hz), 2.60 (2 H, sep, <i>J</i> = 7 Hz)	1.27 (6 H, d, <i>J</i> = 7 Hz), 1.12 (12 H, br d, <i>J</i> = 7 Hz)	
1b	107–108	EtOH	1675	8.26 (1 H, br s), 8.13–7.30 (8 H, m), 7.03 (2 H, s)	2.93 (1 H, sep, <i>J</i> = 7 Hz), 2.63 (2 H, sep, <i>J</i> = 7 Hz)	1.28 (6 H, d, <i>J</i> = 7 Hz), 1.13 (12 H, br d, <i>J</i> = 7 Hz)	
1c	223–224 (223–225) ^e	hexane	1665	7.84 (4 H, s), 7.02 (4 H, s)	2.93 (2 H, sep, <i>J</i> = 7 Hz), 2.59 (4 H, sep, <i>J</i> = 7 Hz)	1.25 (12 H, d, <i>J</i> = 7 Hz), 1.09 (24 H, d, <i>J</i> = 7 Hz)	
1d	215–216	hexane	1670	8.26–7.40 (4 H, m), 6.99 (4 H, s)	2.93 (2 H, sep, <i>J</i> = 7 Hz), 2.54 (4 H, sep, <i>J</i> = 7 Hz)	1.25 (12 H, d, <i>J</i> = 7 Hz), 1.20–0.86 (24 H, m)	
1e	108.5–110	MeOH	1680	7.97 and 7.85 (4 H, AB, <i>J</i> = 9 Hz), 7.03 (2 H, s)	2.93 (1 H, sep, <i>J</i> = 7 Hz), 2.57 (2 H, sep, <i>J</i> = 7 Hz)	2.61 (3 H, s), 1.28 (6 H, d, <i>J</i> = 7 Hz), 1.10 (12 H, br d, <i>J</i> = 7 Hz)	
1f	99–101	EtOH	1705, 1685	8.47 (1 H, s), ^d 8.15 (1 H, d, <i>J</i> = 8 Hz), ^d 7.90 (1 H, d, <i>J</i> = 8 Hz), ^d 7.49 (1 H, t, <i>J</i> = 8 Hz), 7.05 (2 H, s)	2.94 (1 H, sep, <i>J</i> = 7 Hz), 2.59 (2 H, sep, <i>J</i> = 7 Hz)	2.62 (3 H, s), 1.29 (6 H, d, <i>J</i> = 7 Hz), 1.3–0.9 (12 H, br)	
2a	171–173	Et ₂ O-pentane	3490, 1645	7.70 and 7.30 (4 H, AB, <i>J</i> = 8 Hz), 7.84–7.32 (5 H, m), 7.03 (1 H, s), 6.85 (1 H, s)	2.92 (1 H, sep, <i>J</i> = 7 Hz), 2.87 (1 H, sep, <i>J</i> = 7 Hz)	1.47 (3 H, s), 1.17 (6 H, d, <i>J</i> = 7 Hz), 1.23 (3 H, d, <i>J</i> = 7 Hz), 1.16 (3 H, d, <i>J</i> = 7 Hz), 0.86 (3 H, s)	2.68 (1 H, s)
2b	125–126	EtOH	3600, 1660	7.9–7.25 (9 H, m), 7.04 (1 H, s), 6.87 (1 H, s)	2.92 (2 H, sep, <i>J</i> = 7 Hz)	1.46 (3 H, s), 1.27 (6 H, d, <i>J</i> = 7 Hz), 1.16 (3 H, d, <i>J</i> = 7 Hz), 1.13 (3 H, d, <i>J</i> = 7 Hz), 0.87 (3 H, s)	2.60 (1 H, s)
2c	145–146	CH ₂ Cl ₂ -hexane	3580, 1655	7.74 and 7.30 (4 H, AB, <i>J</i> = 8 Hz), 7.03 (3 H, s), 6.87 (1 H, s)	3.03–2.41 (5 H, m)	1.45 (3 H, s), 1.39–0.94 (30 H, m), 0.80 (3 H, s)	2.58 (1 H, s)
2d	142–143	hexane	3550, 1665	7.93–7.26 (4 H, m), 7.00 (3 H, br s), 6.87 (1 H, s)	3.17–2.43 (5 H, m)	1.45 (3 H, s), 1.5–0.7 (30 H, m), 0.78 (3 H, s)	2.57 (1 H, s)
3d ^a	171–172	hexane	3640	7.42 (3 H, s), ^d 6.85 (2 H, s), 6.81 (2 H, s), 6.73 (1 H, br s)	2.85 (2 H, sep, <i>J</i> = 7 Hz), 2.62 (2 H, sep, <i>J</i> = 7 Hz)	1.43 (6 H, s), 1.23 (12 H, d, <i>J</i> = 7 Hz), 0.98 (6 H, d, <i>J</i> = 7 Hz), 0.79 (6 H, s), 0.67 (6 H, d, <i>J</i> = 7 Hz)	2.43 (2 H, s)
3d ^b	101–102	EtOH	3560	7.52 (1 H, s), ^d 7.18–6.90 (5 H, m), 6.86 (2 H, s)	2.91 (4 H, sep, <i>J</i> = 7 Hz)	1.44 (6 H, s), 1.26 (12 H, d, <i>J</i> = 7 Hz), 1.24 (6 H, d, <i>J</i> = 7 Hz), 1.16 (6 H, d, <i>J</i> = 7 Hz), 0.82 (6 H, s)	2.52 (2 H, s)
2e	142–143.5	hexane-C ₆ H ₆	3460, 1670	7.82 and 7.28 (4 H, AB, <i>J</i> = 8 Hz), 7.01 (1 H, s), 6.84 (1 H, s)	3.20–2.57 (2 H, m)	2.54 (3 H, s), 1.46 (3 H, s), 1.28 (6 H, d, <i>J</i> = 7 Hz), 1.19 (3 H, d, <i>J</i> = 7 Hz), 1.15 (3 H, d, <i>J</i> = 7 Hz), 0.81 (3 H, s)	2.77 (1 H, s)
2f	105–106	EtOH	3600, 1690	7.90–7.05 (4 H, m), 7.00 (1 H, s), 6.80 (1 H, s)	3.10–2.40 (2 H, m)	2.54 (3 H, s), 1.46 (3 H, s), 1.27 (6 H, d, <i>J</i> = 7 Hz), 1.20 (3 H, d), 1.15 (3 H, d), 0.80 (3 H, s)	2.60 (1 H, s)

^a Higher melting isomer. ^b Lower melting isomer. ^c Usually the two small peaks on both sides of the septet could not be seen under normal run conditions. ^d Finely split (*J* = 1.5–2 Hz). ^e Reference 19.

Table VI. Summary of Analyses

compd	calcd, %		found, %	
	C	H	C	H
1a	84.42	7.82	84.59	7.85
1b	84.42	7.82	84.08	7.77
1d	84.71	9.35	84.77	9.42
1e	82.24	8.63	82.40	8.62
1f	82.24	8.63	82.10	8.81
2a	84.42	7.82	84.14	7.99
2b	84.42	7.82	84.55	7.47
2c	84.71	9.35	84.98	9.62
2d	84.71	9.35	84.86	9.22
3d ^a	84.71	9.35	84.92	9.13
3d ^b	84.71	9.35	84.69	9.34
2e	82.24	8.63	82.51	8.78
2f	82.24	8.63	82.57	8.84

^a Higher melting isomer. ^b Lower melting isomer.

(28% yield) of another stereoisomer (a lowering melting isomer) of 3d.

Properties and analyses of the benzocyclobutenols 2a-f and 3d are listed in Tables V and VI.

Quantitative Photolyses. Irradiations were done at 25 °C, after degassing the solution in 17 × 120 mm Pyrex tubes by four freeze-thaw cycles below 10⁻² mmHg, on a merry-go-round apparatus (Riko RH 400-10 W) by 313-nm light which was isolated from a 400-W high-pressure mercury lamp with a K₂CO₃ (1.3%)-K₂CrO₄ (0.13%) filter solution. The benzocyclobutenols produced were analyzed by HPLC. Methyl-2-naphthyl ketone was used as the internal standard. Two par-

allel runs for quantum yield measurements agreed within experimental error (±10%).

An authentic sample of 1,3-diisopropyl-10,10-dimethylantrone (4) was prepared by extended irradiation (15 h) of a mixture of 2 (X = H) (750 mg) and acetophenone (2.02 g) in benzene (250 mL) under preparative photolysis conditions. After evaporation of the solvent, the residue was separated by column chromatography on silica gel (70 g). Elution with petroleum ether (2400 mL) and then with hexane (1200 mL) afforded successively 40 mg (9% yield) of 4, acetophenone (1.7 g), and recovered 2 (X = H) (295 mg). The yield of 1 (X = H) was below 1% (by HPLC). Anthrone 4 resisted crystallization even after repeated purification with preparative TLC, but its NMR and IR spectra were close to those of 1-isopropylantrone prepared by established methods:²¹ NMR (CDCl₃) δ 8.19 (1 H, d with fine splitting, *J* = 7.5 Hz, *J'* = 1.7 Hz, 8-H), 7.64-7.33 (3 H, m, 5- to 7-H), 7.39 and 7.30 (each peak equals 1 H, d, *J* = 1.8 Hz, 2- and 4-H), 4.41 (1 H, sep, *J* = 7 Hz, 1-CH(CH₃)₂), 2.99 (1 H, sep, *J* = 7 Hz, 3-CH(CH₃)₂), 1.72 (6 H, s, 10-Me), 1.33 and 1.31 (each peak equals 6 H, d, *J* = 7 Hz, 1- and 3-CH(CH₃)₂); IR (neat) 1660 cm⁻¹ (C=O); high-resolution mass spectrum (calcd for C₂₂H₂₆O, *m/e* 306.1984), *m/e* 306.1986.

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Registry No. 1a, 84369-66-4; 1b, 84369-67-5; 1c, 76893-85-1; 1d, 84369-68-6; 1e, 84369-69-7; 1f, 84369-70-0; 2a, 84369-71-1; 2b, 84369-72-2; 2c, 84369-73-3; 2d, 84369-74-4; 2e, 84369-75-5; 2f, 84369-76-6; *dl*-3d, 84369-77-7; *meso*-3d, 84369-78-8.

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Aromatic Substitution in the Gas Phase. Intramolecular Selectivity of the Reaction of Aniline with Charged Electrophiles

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Abstract: The intramolecular selectivity of the electrophilic reactions of radiolytically formed C₂H₅⁺, *i*-C₃H₇⁺, *t*-C₄H₉⁺, (CH₃)₂F⁺, and CH₃CO⁺ cations with aniline has been investigated in the gas phase at nearly atmospheric pressure. Under conditions of kinetic control of products, the reactivity of the N atom and of the aromatic ring is comparable, a mixture of ring- and N-substituted products being invariably formed in proportions that depend on the nature of the electrophile. The relative rate of N-substitution increases in the order: C₂H₅⁺ ≈ *i*-C₃H₇⁺ < (CH₃)₂F⁺ < *t*-C₄H₉⁺ < CH₃CO⁺. The positional selectivity of the gaseous electrophiles, except CH₃CO⁺, is characterized by predominant ortho substitution.

Aniline is a typical ambient nucleophile whose reactivity toward gaseous cations has been the subject of numerous recent studies, concerning in particular its preferred protonation site. The combination of various mass spectrometric techniques with theoretical methods¹⁻¹² has led to the accurate determination of the

proton affinity (PA) of aniline and to the conclusion that the amine is a nitrogen base in the gas phase as well as in solution. However, the stabilities of the ring- and N-protonated isomers are estimated to be very close, probably within a few kcal mol⁻¹.

These results, and the meager evidence available on ion-molecule reactions of aniline other than proton transfer,¹³ bear exclusively on the *thermodynamic* aspects of the problem; e.g.,

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