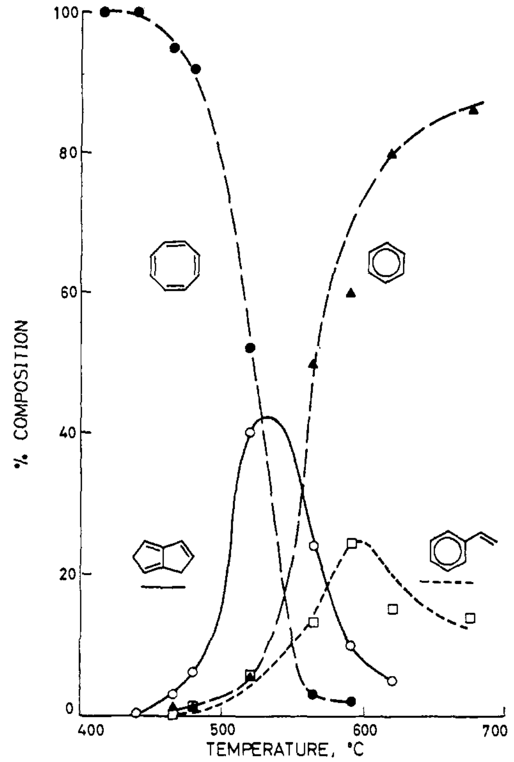

Figure 1. Cyclooctatetraene pyrolysis: product composition as a function of temperature.

Stiles[7] on diphenyldibenzocyclooctatetraenes and of Schwab[8] on 1,8-dicarbomethoxycyclooctatetraene.

(8) L. O. Schwab, unpublished work.

(9) Alfred P. Sloan Research Fellow, 1967–1969.

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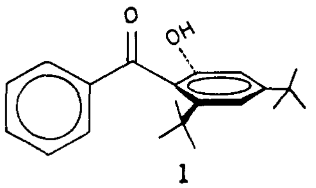
2-Hydroxy-4,6-di-*t*-butylbenzophenone Photoreactivity

Sir:

The steric requirements of the *t*-butyl groups in 1[1] force the molecule to exist predominantly in a conformation in which the planes of the two aromatic rings are essentially perpendicular to one another.[2] As



1

is evidenced by its infrared and ultraviolet spectra, this geometrical restriction precludes the existence of both intramolecular hydrogen bonding[3] and low-energy charge-transfer transitions (<40,000 cm^{-1}) in **1**. Since both conditions are believed to provide mechanisms for rapid deactivation of excited states of 2- and 4-hydroxybenzophenone (**2** and **3**),[4,5] and other series of compounds,[6] it was of interest to determine the effect, if any, of the 2-hydroxy group on the photoreactivity of **1** relative to **2**, **3**, and benzophenone (**4**).

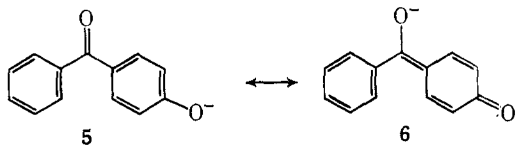
The electronic absorption and emission spectra of **1** indicate both its lowest singlet and triplet excited states to have an n,π* configuration. The former exhibits a broad maximum at λ ~3100 Å (ε ~100),[1] while the phosphorescence of **1** (0–0 band ~25,600 cm^{-1}) in an EPA glass at 77°K is bright with a mean lifetime of 2×10^{-4} sec. The singlet–triplet splitting for **1** (~5000 cm^{-1}) is also characteristic of that for n,π* states. On the basis of these spectral data one would predict efficient intersystem crossing from the lowest excited singlet state of **1**, generating a reactive n,π* triplet state. The observed photoreactivity of **1** is not in accord with this simple picture. Quantum yields measured for the total loss of **1** subsequent to irradiation[7] in 2-propanol and in methylcyclohexane are compared with those reported for **2–4** in Table I.

Table I. Comparison of Photoreactivity of **1–4**

Compd	Φ_{ROH}	Φ_{RH}
1	2×10^{-3}	1.3×10^{-3}
2[a]	7×10^{-3}	*c*
3[b]	2×10^{-2}	0.9
4[b]	1.0	0.5

[a] Taken from ref 8. [b] Taken from ref 5. [c] Not reported.

Porter[5] has related the low photoreactivity of **3** in alcoholic media to the high acidity of its charge-transfer excited singlet state (pK_a^* = −3). He proposed that proton transfer to the solvent competes favorably with intersystem crossing from this state. The phenolate anion (**5**) thus generated is unreactive with respect to hydrogen abstraction due to contribution of structure **6** to its resonance hybrid. *Structures of the type* **6** *are*



5 **6**

sterically inhibited in **1**. In hydrocarbon media, the energies of the charge-transfer singlet and triplet states of **3** are raised, and a reactive n,π* triplet is populated.

The low photoreactivity of **2** has been related to reversible enolization[9,10] and to the charge-transfer

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(1) R. A. Finnegan and D. Knutson, *Chem. Ind.* (London), 1837 (1965).

(2) A. T. Shulgin and H. O. Kerlinger, *Chem. Commun.*, 249 (1966).

(3) The O–H stretching vibration of **1** has been reported[2] to be a partially resolved doublet ($\bar{\nu}_{OH}^{CCl_4}$ 3609, 3588 cm^{-1}). The authors assign the 3588-cm^{-1} band to a conformer of **1** in which there is a weak intramolecular hydrogen bond between the phenolic hydrogen and the π bond of the adjacent carbonyl group. The frequency interval between the free O–H and the bonded O–H in **1** corresponds to an energy separation of ~0.05 kcal. Nonbonded interactions in *ortho*-substituted phenols are known to result in splittings of the O–H stretching frequency of this order of magnitude. In the context of this paper, intramolecular hydrogen bonding refers to bonding interactions of the order of 1 kcal or greater.

(4) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963).

(5) G. Porter and P. Suppan, *ibid.*, **61**, 1664 (1965).

(6) J. R. Merrill and R. G. Bennett, *J. Chem. Phys.*, **43**, 1410 (1965).

(7) All photolyses were carried out in the absence of oxygen with a 1000-W xenon arc filtered to transmit light of wavelengths 2400–3400 Å. Analyses were carried out by glpc. Quantum yields are accurate to ±30%.

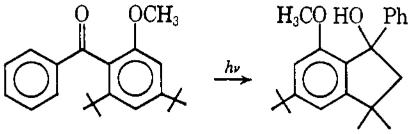
(8) T. S. Godfrey, G. Porter, and P. Suppan, *Discussions Faraday Soc.*, 194 (1965).

configuration of its excited states.[11] The role of intramolecular hydrogen bonding in the deactivation of excited states of **2** is not clear.[11] However, intramolecular hydrogen bonding has been proposed to provide a deactivation mechanism for excited states of amidophenylbenzotriazoles.[6] Since all the conditions postulated to explain the high photostability of **2** are sterically precluded in **1**, we ask: what is the mechanism of deactivation of excited states of **1**?

Using the technique of Weller[12] the pK_a^* for 1 in its lowest excited singlet state was estimated at ~ -4 to -5. Such a low value for pK_a^* suggests that rapid deprotonation competes with intersystem crossing from the n,π^* singlet state of **1**. The fact that **1** is photostable in hydrocarbon media demonstrates that the solvent is not involved as an accepting base. We propose that, subsequent to population of its n,π^* singlet state, **1** undergoes *reversible intramolecular proton transfer* of its phenolic hydrogen to the neighboring carbonyl oxygen. The zwitterionic species **7** formed in this reaction would not be expected to abstract a hydrogen atom from solvent but rather collapse to **1**.

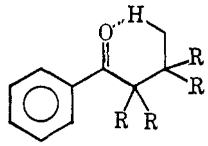
7

An alternative explanation for the low photoreactivity of **1** is steric inaccessibility of the carbon group. This was dismissed by determining the quantum yield for photolysis of 2-methoxy-4,6-di-*t*-butylbenzophenone (**8**) in ethanol to be 0.5. The major product formed by irradiation of **8** in ethanol is the indanol **6**. No carbinol or pinacol reduction products were isolated. Compound **9** is presumably formed by intramolecular hydrogen abstraction from the *o*-*t*-butyl group of **8** followed by cyclization of the diradical thus generated. It is this intramolecular cyclization reaction with which reversible proton transfer in **1** must compete.



8 **9**

Our results on **1** prompt the question as to what contribution intramolecular hydrogen bonding makes to the high photostability of **2**. Does the intramolecular hydrogen bond itself provide an additional deactivation mechanism, or is reversible intramolecular proton transfer the only significant deactivation process for excited states of this class of compounds? Further work on the clarification of this point is anticipated on compounds of the general structure **10**. In **10**, effects directly attributable to intramolecular hydrogen bonding can be observed in the absence of complications due to low-lying charge-transfer states and to reversible proton-transfer reactions.



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[9] J. N. Pitts, Jr., H. W. Johnson, and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

[10] G. Porter and P. Suppan, *Pure Appl. Chem.*, **9**, 499 (1964).

[11] G. Porter and P. Suppan, *Trans. Faraday Soc.*, **62**, 3375 (1966).

[12] A. Weller, "Progress in Reaction Kinetics," G. Porter, Ed., Pergamon Press, New York, N. Y., 1961, pp 189–191.

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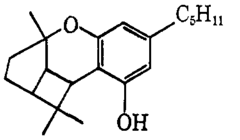
Constituents of Hashish. A Novel Reaction of Olivetol with Citral in the Presence of Pyridine. Total Synthesis of *dl*-Cannabicyclol and *dl*-Cannabichromene[1]

Sir:

The components of hashish have received renewed interest in recent years.[2b] A synthesis of *dl*-$\Delta^{1(6)}$-3,4-*trans*-tetrahydrocannabinol (**3**) and $\Delta^{4(8)}$-isotetrahydrocannabinol (**4**) has been effected by condensation of olivetol (**1**) with citral (**2**) in the presence of 10% boron trifluoride etherate in benzene solution.[2c,d] However, when the reaction was carried out under the milder acidic conditions of 0.0005 *N* HCl in ethanol[2c] or of 1% boron trifluoride etherate in methylene chloride,[2b] *dl*-Δ^1-3,4-*cis*- (**6**) and *dl*-Δ^1-3,4-*trans*-THC (**5**) were isolated.

We now wish to report in this communication that the reaction of olivetol (**1**) with citral (**2**) in pyridine[3] takes a different course which provides a useful, simple, one-step synthesis of the racemic modifications of two

[1] Since submission of our paper, the synthesis of cannabicyclol and cannabichromene has been reported by L. Crombie and R. Ponsford, *Chem. Commun.*, 894 (1968). Another synthesis of cannabichromene has also been reported by G. Cardillo, R. Cricchio, and L. Merlini, *Tetrahedron*, **24**, 4825 (1968). In Crombie and Ponsford's paper a new structure was proposed for cannabicyclol. This structure does not satisfactorily explain (a) the high-field methyl signal at 0.78 ppm in the nmr; (b) the fragment at *m/e* 232 in the mass spectral data; and (c) its formation from **10** on mechanistic grounds. We therefore suggest that in the absence of further experimental data the structure and stereochemistry as suggested by Korte[2a] and Mechoulam[2b] should not be discarded at the present time.



[2] (a) U. Claussen, F. V. Spulak, and F. Korte [*Tetrahedron*, **24**, 1021 (1968)] have isolated from hashish a crystalline compound, mp 144–146°, $[\alpha]^{20}D$ $-3°$, to which they have given the structure **9** on the basis of its nmr and mass spectral data and called it cannabipinol. They did not prove the identity of their cannabipinol with Mechoulam's[2b] cannabicyclol. However, Professor Korte (private communication) has kindly informed us that his sample and ours are the same as shown by ir (solution), mixture melting point, and mass spectrum. Hence this establishes the identity of cannabicyclol and cannabipinol. (b) R. Mechoulam and Y. Gaoni, *Fortschr. Chem. Org. Naturstoffe*, **25**, 175 (1967). (c) E. C. Taylor, K. Lenard, and Y. Shvo, *J. Am. Chem. Soc.*, **88**, 366 (1966). (d) Y. Gaoni and R. Mechoulam, *ibid.*, **88**, 5673 (1966).

[3] (a) C. E. Berkoff and L. Crombie, *J. Chem. Soc.*, 3734 (1960). (b) While our work was in progress, the potential synthetic utility of this reaction was also pointed out in a recent publication: L. Crombie and R. Ponsford, *Chem. Commun.*, 368 (1968).