

# Chemical Communications

NUMBER 9/1966

11 MAY

## The Carbonyl Double Bond: A New Hydrogen Bond Receptor

By A. T. SHULGIN and H. O. KERLINGER

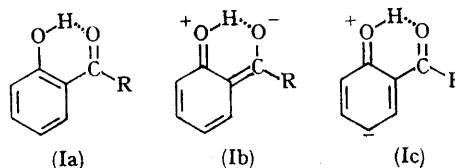
(The Dow Chemical Company, Walnut Creek, California)

THE hydrogen bond that can exist between phenols and ketones has been extensively studied. In intermolecular examples of this interaction, the participating molecules can align themselves in favourable orientation for bonding and the oxygen atom of the ketone, as its most negative component, always serves as the hydrogen bond receptor. In intramolecular instances of hydrogen bonding of this type, a severe limitation is encountered by the restriction of the phenolic group to the plane of the aromatic ring. Nonetheless, when the carbonyl group is located in a manner that allows a six-membered ring to form (as in Ia), a very strong bond occurs.<sup>1</sup> Even as one displaces the carbonyl oxygen slightly from the plane of the aromatic ring [R in (Ia) going from H to Ph<sup>2</sup>], the stabilization provided by quinonic resonance forms such as (Ib) and (Ic) is still adequate to maintain a close association. Consequently, the  $\nu_{\text{OH}}$  absorption in the infrared has been found invariably to be broad and shifted by several hundred wave numbers to lower frequencies, and there is a corresponding decrease in the  $\nu_{\text{C}=\text{O}}$  of perhaps 30  $\text{cm}^{-1}$ .

A recent report<sup>3</sup> has described such an *ortho*-hydroxybenzophenone (II) as a major product of the photo-Fries rearrangement of 3,5-di-*t*-butylphenyl benzoate. However, the spectral properties of this compound included a  $\nu_{\text{OH}}$  at 3448  $\text{cm}^{-1}$ .

• The hydrogen that is located *para* to the hydroxyl group and is a triplet in both 3,5-di-*t*-butylphenol and its benzoate ester, becomes a doublet in (II).

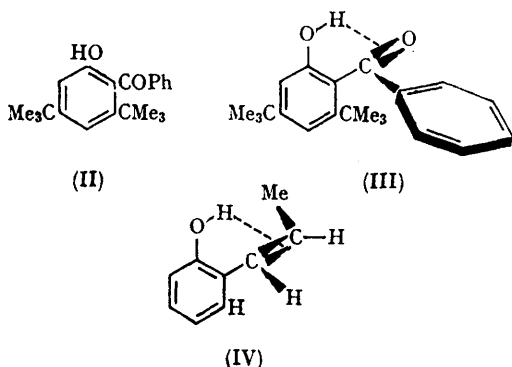
and a  $\nu_{\text{C}=\text{O}}$  at 1648, both highly suggestive of an unbonded hydroxy-ketone. It was apparent that either the Fries rearrangement had resulted in *para*- rather than *ortho*-substitution (*i.e.*, misassignment of structure) or that the adjacent *t*-butyl group in (II) disrupts the conventional O-H  $\cdots$  O=C hydrogen bond.



The procedure described by Finnegan and Knutson<sup>3</sup> was repeated, and a hydroxy-ketone was obtained that agreed in all particulars with their product. As the high-resolution n.m.r. analysis of the aromatic protons of (II) left no doubt but that the *ortho*-assignment was correct,\* a study was made of the abnormal hydrogen bond system that is represented here.

An infrared spectrum of the  $\nu_{\text{OH}}$  area was obtained in  $\text{CCl}_4$  employing a cell (1  $\text{cm}.$ ) and concentration ( $10^{-2}\text{M}$ ) that precluded intermolecular phenomena. A sharp band at 3609  $\text{cm}^{-1}$

and the absence of broad absorption in the 3200—3300  $\text{cm}^{-1}$  region indicate a completely unassociated phenolic hydroxyl group. There is a partially resolved, concentration-independent band present at 3588  $\text{cm}^{-1}$ , and it can only represent some bonded conformer involving a very weak base. Of the three distinct basic regions in the benzoyl



group (the oxygen, the carbonyl  $\pi$ -cloud, and the aromatic  $\pi$ -cloud), only the carbonyl oxygen affords a base of sufficient strength to overcome the resonance stabilization that constrains the phenolic hydroxyl group to the plane of the ring.<sup>4</sup> In these instances, the absorption band associated with this bond is broadened and shifted 100—200 wave numbers to lower frequencies, a transformation qualitatively similar to the near-planar bonding situation represented in (Ia). It remains,

then, that the hydroxyl group indeed stays in-plane and the benzoyl group is placed in a non-conjugated, lateral, position by steric interaction with the adjacent *t*-butyl group, as illustrated in (III).

As neither carbonyl oxygen nor the yet more distal aromatic  $\pi$ -cloud is available to the hydroxyl group, the olefin-like field that lies between the carbon and the oxygen of the carbonyl system must be considered as the functional base in this bond. Striking confirmation of this assignment is found in the spectrum of *ortho-cis*-propenyl-phenol (IV).<sup>5</sup> The infrared absorption of this material displays again an unbonded hydroxyl (at 3610  $\text{cm}^{-1}$ , the *trans*-configuration of the planar O—H residence<sup>6</sup>) and two *cis*-conformations representing two out-of-plane positions of stability of the olefin double bond (at 3585  $\text{cm}^{-1}$  and at 3548  $\text{cm}^{-1}$ ).<sup>5</sup> The one of these that leads to absorption at 3585  $\text{cm}^{-1}$  presents an electronic environment to the bonding hydroxyl group that is identical to that found in (III). This emphasizes the narrowness of the cone in which a hydrogen bond can be formed for here, the strength and character of the association between an aromatic (planar) O—H group and an adjacent (but not of the same plane) olefinic  $\pi$ -system is quite independent of the identity of the atom found in the  $\beta$ -position.

Experiments with compounds of similar but less severe steric constraint are currently being pursued.

(Received, March 11th, 1966; Com. 151.)

<sup>1</sup> L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, 1958.

<sup>2</sup> E. J. Mauconi, W. F. O'Connor, and W. F. Forbes, *J. Amer. Chem. Soc.*, 1960, **82**, 5454; R. A. Nyquist, *Spectrochim. Acta*, 1963, **19**, 1655.

<sup>3</sup> R. A. Finnegan and D. Knutson, *Chem. and Ind.*, 1965, 1837.

<sup>4</sup> L. J. Bellamy and R. L. Williams, *Proc. Roy. Soc.*, 1960, *A*, **254**, 119.

<sup>5</sup> A. W. Baker and A. T. Shulgin, *Spectrochim. Acta*, 1964, **20**, 1953.

<sup>6</sup> L. Pauling, *J. Amer. Chem. Soc.*, 1936, **58**, 94.