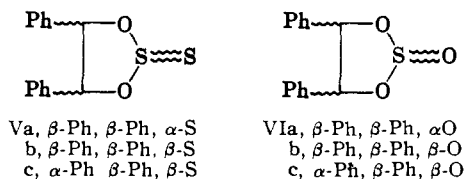(aromatic protons, complex multiplet entered at 7.05 p.p.m., methenyl protons, sharp singlet at 6.32 p.p.m.), and a minor isomer, Vb,[9] m.p. 89–90° (aromatic protons, single peak at 7.11 p.p.m., and methenyl protons, singlet at 5.76 p.p.m.). Each isomer gave the correct analysis and molecular weight, and each yielded *meso*-hydrobenzoin on desulfurization. Conversion of *meso*-hydrobenzoin to the cyclic sulfite with thionyl chloride

Va, β-Ph, β-Ph, α-S
  b, β-Ph, β-Ph, β-S
  c, α-Ph β-Ph, β-S

VIa, β-Ph, β-Ph, αO
  b, β-Ph, β-Ph, β-O
  c, α-Ph, β-Ph, β-O

and pyridine gave a sulfite mixture VIa,b consisting of approximately nine parts of a major isomer, VIa, m.p. 130–131°,[10] and one part of a minor isomer, VIb, m.p. 129–131°. P.m.r. spectra of the major and minor sulfite isomers were identical in character (major isomer, complex aromatic protons at ~7.04 p.p.m., methenyl protons, singlet at 6.14 p.p.m.; minor isomer, sharp aromatic signal at 7.13 p.p.m. with methenyl singlet at 5.84 p.p.m.) with Va and Vb, respectively.

dl-Hydrobenzoin was converted to the thionosulfite Vc, m.p. 78–80° (correct analysis for $C_{14}H_{12}O_2S_2$), and the sulfite VIc, m.p. 85–86°.[10a,c] Single compounds were obtained in each case. Their p.m.r. spectra were essentially equivalent with each showing the expected nonequivalence of methenyl protons.

The isolation of individual sulfite and thionosulfite isomers and the striking similarities between the two classes constitutes compelling evidence for the existence of branch-bonded thiono analogs of cyclic sulfites.

(10) (a) C. C. Price and G. Berti, *J. Am. Chem. Soc.*, **76**, 1211 (1954); (b) Z. Kitasato and C. Sone, *Ber.*, **64**, 1142 (1931); (c) D. Reulos and S. LeTellier, *Compt. rend.*, **217**, 698 (1943).

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## Formation of Phenyl Radical by Heterolysis of N-Phenyl-N'-benzoyldiimide[1]

Sir:

We wish to report that treatment of solutions of N-phenyl-N'-benzoyldiimide, C_6H_5—N=N—COC_6H_5 (I), with acid or base leads to free phenyl radical, presumably *via* phenyldiimide, C_6H_5N=NH (II). Compound I is thermally stable[2] at 135° and may be crystallized from ethanol.[3] We have found that the presence of 0.01 N hydrogen chloride led to rapid decomposition of 0.006 M I in methanol, 90% yield of nitrogen, 85% yield of methyl benzoate, and *ca.* 55% yield of benzene; 0.01 N NaOH also led to rapid heterolysis. At higher initial concentration (1.6 M) of I, the yields of

(2) H. Wieland, H. vom Hove, and K. Borner, *Ann.*, **446**, 31 (1926).

(3) G. Pouzio and G. Charrier, *Gazz. chim. ital.* **39**, I, 596 (1909).

methyl benzoate and benzene fell to 43 and 12%, respectively, as a considerable part of the phenyldiimide and/or phenyl radical added to I, preventing its heterolysis, and led to a combined 26% yield of N,N-diphenyl-N'-benzoylhydrazine,[4] $(C_6H_5)_2NNHCOC_6H_5$ (III), m.p. 189–191°, and N,N'-diphenyl-N-benzoylhydrazine,[5] $C_6H_5NHN(C_6H_5)COC_6H_5$ (IV), m.p. 136–138°.

At intermediate initial concentration (0.2 M) of I, acid-catalyzed methanolysis also led to lower yields of methyl benzoate (45%) and benzene (*ca.* 15%). However, addition of 2 M fumaric acid led again to a high yield of methyl benzoate (75%), but to a still lower yield of benzene (4%). The fumaric acid competed with I for phenyldiimide and phenyl radical, allowing extensive methanolysis of I and formation of methyl benzoate, diverted phenyldiimide and phenyl radical from formation of benzene, and led to phenylsuccinic acid, m.p. 165–167°, 46% yield.

Acid-catalyzed heterolysis of 0.2 M I in 2-propanol led to a 32% yield of 2-propyl benzoate, 35% nitrogen, 26% benzene, 16% acetone, and to compounds III and IV. In 3:1 carbon tetrachloride–methanol, 0.16 M I led to a 58% yield of methyl benzoate, 40% chlorobenzene, 19% chloroform, and a low yield of benzene. In benzene containing 3% of methanolic hydrogen chloride, 0.17 M I led to a 41% yield of methyl benzoate and to a 38% yield of biphenyl. In 3:1 nitrobenzene–methanol, 0.18 M I led to a 59% yield of methyl benzoate, 10% of benzene, and to a 33% combined yield of nitrobiphenyls, of which the 2-, 3-, and 4- isomers were obtained in the ratio 31:8:61. Finally, acid methanolysis of 0.075 M I in acrylonitrile led to exothermic polymerization, 65% conversion to polyacrylonitrile.

Methanolysis probably occurs *via*

$$C_6H_5-N=N-COC_6H_5 + CH_3OH \xrightarrow[OH^-]{H^+}$$
$$I$$
$$C_6H_5N=NH + C_6H_5CO_2CH_3 \quad (1)$$
$$II$$
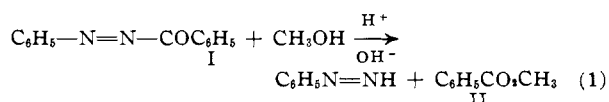
Phenyldiimide may add to unreacted I, leading to III and IV, or to fumaric acid, or it may decompose within a solvent cage to form benzene. It may also lead to phenyl radical, the course of which reaction will be discussed in a later publication. The phenyl radical may then (i) add to I leading to III and IV; (ii) add to fumaric acid and lead to phenylsuccinic acid; (iii) abstract hydrogen from alcohol, forming benzene and leading 2-propanol to acetone; (iv) abstract chlorine from carbon tetrachloride; (v) arylate benzene and nitrobenzene, leading in the latter case to a predominance of *o*- and *p*-nitrobiphenyls; and (v) initiate polymerization.

Aryl radicals may thus be produced in satisfactory yield from thermally stable N-acyl-N'-aryldiimides by simple treatment with dilute acid or base at room temperature in homogeneous medium, conditions which may make them more desirable than other sources of free radicals, diazonium salts,[6] diazohydroxides,[7] and diazoacetates,[7] acylarylnitrosoamines.[8]

(4) E. Fischer, *Ann.*, **190**, 178 (1878).

(5) J. Biehringer and A. Busch, *Ber.*, **36**, 139 (1902).

(6) H. A. H. Pray, *J. Phys. Chem.*, **30**, 1417, 1477 (1926); W. A. Waters, *J. Chem. Soc.*, 864 (1939).

(7) M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, **46**, 2339 (1924).

(8) W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1797 (1934).

arylazotriphenylmethanes,[9] and, under certain circumstances, diacyl peroxides.[10]

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(10) H. Gelissen and P. H. Hermans, Ber., 58, 285 (1925).

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Solvent Effects on the C^{13} Chemical Shift of the Substituted Carbon Atom of Phenol[1]

Sir:

A recent investigation of the effect of solvents on the C^{13} chemical shift of the carbonyl group of acetone[2] and other carbonyl-containing compounds[3] indicates that the shift is quite sensitive to an environment consisting of proton donors, relatively insensitive to environment if proton donors are absent, and may provide a useful tool for the study of acidic and hydrogen-bonding properties of solvents. In the hope of developing an analogous means of studying the basic properties of solvents, we have undertaken a solvent-shift study of the C^{13} magnetic resonance spectra of phenol.

The C^{13} spectra of phenol were obtained in natural abundance in 1:4 mole fraction solutions of phenol in several reagent grade or Eastman White Label solvents. A measuring frequency of 15.1 Mc./sec. and the rapid passage dispersion mode technique described previously by Lauterbur[4] were employed. Shifts were measured in a concentric-sphere sample container,[5] to eliminate bulk susceptibility effects, with respect to an external reference of a saturated aqueous $NaO_2C^{13}CH_3$ solution in the center sphere, using the side-band technique.

The observed C^{13} shifts of the substituted carbon atom, and the carbon atoms situated *ortho*, *meta*, and *para* to the substituted carbon atom, are presented in Table I. They may be considered reliable to about ±0.5 p.p.m. In those cases where the assignment of the resonance lines was not straightforward due to weak and/or overlapping signals, reliable data could not be obtained readily and are not presented. Inspection of the table reveals that the shifts of *meta* carbons vary only slightly with solvent, with no obvious trends apparent. The variations of the *ortho* and *para* shifts with solvent are relatively small and do not appear to follow a recognizable pattern, except that in the most basic media they become interchanged with respect to their values in less basic solvents. Probably the most interesting set of shifts in this work are those of the substituted carbon atom and our discussion will be limited primarily to those shifts. They span a total range of 12.7 p.p.m., the largest positive shift occurring in cyclohexane solution and the largest negative shift in a system consisting of phenol, sodium ethoxide, and ethanol in mole proportions of 1:1:4, in which the phenol exists in the form of solvated phenoxide ion.

Table I shows that the resonance line for the substituted carbon atom experiences a definite trend to lower field as the basicity of the solvent increases. In

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TABLE I

C^{13} CHEMICAL SHIFTS OF PHENOL IN 1:4 MOLE FRACTION SOLUTIONS IN SEVERAL SOLVENTS (P.P.M. WITH RESPECT TO BENZENE)

Solvent	Carbon-1	*ortho*	*meta*	*para*	$\Delta\nu$, cm.$^{-1a}$
Cyclohexane	−26.9	12.6	−1.8	7.9	
Carbon tetrachloride	−27.0	11.9	−1.5	6.9	0
Benzotrifluoride	−27.1				
Nitromethane	−27.2				
Benzene	−27.9				24
Ethyl acetate	−28.4	13.5	−0.7	9.6	51
Acetonitrile	−28.6	12.9	−1.5	8.8	87
Diethyl ether	−29.1	12.9	−1.3	9.2	96
Dioxane	−28.9	13.1	−1.1	9.4	111
Tetrahydrofuran	−29.0	14.6	0.0	10.1	117[b]
Acetone	−29.2	12.7	−1.8	8.2	121
Dimethyl sulfoxide	−29.8	13.2	−1.5	8.9	158[c]
t-Butylamine	−30.1				
Tri-*n*-butylamine	−30.3	11.3	−0.3	11.3	243[d]
Diethylamine	−30.6	11.1	−0.4	11.1	268[d]
Ethanol–sodium ethoxide[e]	−39.6	8.2	−1.9	13.6	

[a] Frequency shift of O–D stretching band of CH_3OD in these solvents, taken from ref. 7 unless otherwise noted. [b] Reference 8. [c] Reference 9. [d] Reference 10. [e] Sample consisted of phenol, sodium ethoxide, and ethanol in mole ratios of 1:1:4.

the case of highly basic solvents, this trend can be understood most simply in terms of changes in the position of the rapid multiple equilibrium

$$(1/x)(C_6H_5OH)_x + B \rightleftharpoons C_6H_5OH \cdots B \rightleftharpoons C_6H_5O^- + HB^+$$
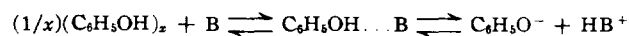
to favor the proton-transfer product, solvated phenoxide ion, as the strength of the base B increases. However, in moderately basic or weakly basic solvents, the equilibrium concentrations of phenoxide ion would be too small to influence the observed weighted-average chemical shifts significantly. In this case the most realistic interpretation of the trend to lower fields with increasing solvent basicity appears to be the increasing influence of hydrogen bonding of phenol to solvent. Thus, the position of the above equilibrium and its consequent effect on the observed chemical shift depends on the ability of solvent to form a hydrogen-bonded complex with phenol and thus compete with the phenol self-association state which is predominant in inert and weakly basic solvents at the concentrations employed in this study.[6]

For comparison, Table I includes solvent shifts, $\Delta\nu$, of the O–D stretching frequency of CH_3OD, which Gordy[7] and Tamres and Searles[8−10] have used as indices of the basic strengths of solvents with respect to hydrogen bonding to methanol. Qualitative correlations can also be made with other reported measures of solvent basicities.[11−13] This apparent relationship of solvent shift in weakly and moderately basic solvents to the ability of the solvent to accept a proton in a hydrogen-bonded complex is consistent with the fact

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