

higher than any found for phosphorescent hydrocarbons.^{2,13,14b} In the nitrenes there are two unpaired electrons at least partially on the same atom. Such localization causes considerable interaction. This arrangement is forbidden in the excited states of aromatic hydrocarbons where there is only one available atomic orbital in each atom. In addition, these values are higher than any likely to be required for diphenylmethylene.³ In the latter the presence of the second phenyl group aids delocalization, and the smaller nuclear charge of the carbon atom permits a larger inter-electronic separation. Both effects should reduce the spin-spin dipole energy and lead to smaller values of D .

(16) Computations by J. Higuchi have given values of D of 1.0 and 1.8 cm.⁻¹ for CH₂ and NH, respectively (J. Higuchi, private communication).

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RECEIVED JULY 7, 1962

REACTION OF DIPHENYLACETYLENE WITH NICKEL SULFIDES

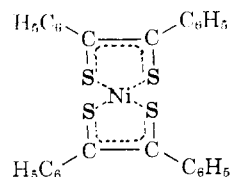
Sir:

The hypothesis that W. Steinkopf's well-known synthesis of thiophene from acetylene and pyrite¹ might yield organometallic complexes if conducted under milder conditions has led us to investigate the reaction of metallic sulfides with acetylenes. Technical-grade nickel sulfide, prepared by the addition of ammonium sulfide to neutral or slightly acidic solutions of a nickel salt, usually contains a non-stoichiometric excess of sulfur.² This nickel sulfide was found to react with diphenylacetylene in toluene in a closed tube at 160° to produce large amounts of tetraphenylthiophene. If, however, the reaction was conducted at 120°, the toluene solution became dark green within 24 hours and upon cooling deposited a nearly black, crystalline complex (I) of composition NiC₂₈H₂₀S₄ (Calcd. C, 61.89; H, 3.70; S, 23.61; Ni, 10.80; mol. wt. 543. Found C, 61.9; H, 3.7; S, 23.5; Ni, 10.5; mol. wt. 578). Under these conditions only small amounts of tetraphenylthiophene are formed suggesting that I is an intermediate in the tetraphenylthiophene formation. I is completely stable to air and decomposes at 290° into nickelous sulfide, sulfur and (exclusively) 2-phenylthianaphthene. Reduction with HI-phosphorus in acetic acid at 140° yields mainly desoxybenzoin and small amounts of bibenzyl. Reaction with diphenylacetylene at 140° in toluene afforded up to 76% of the theoretical amount of tetraphenylthiophene. Diethylacetylenecarboxylate reacted even at 80° producing diethyl 4,5-diphenylthiophene-2,3-dicarboxylate (m.p. 98°). I is moderately soluble in most nonpolar solvents, forming deeply green solutions. Enhanced solubility in bases such as pyridine and piperidine and a color change to brown-red suggest the formation of complexes of I with solvent molecules. Indeed, labile bis-adducts of both bases were isolated in crystalline form. The

(1) W. Steinkopf and G. Kirchhoff, *Ann.*, **403**, 1 (1914); W. Steinkopf, *ibid.*, **403**, 11 (1914).

(2) E. Dönges, *Z. Naturforschung*, **1**, 221 (1946).

proton magnetic resonance spectrum of I in CS₂ solution consists of but one signal of the phenyl protons. From these observations a structure is deduced in which a nickel atom is surrounded by two molecules of dithiobenzil in a square planar arrangement.



Magnetic measurements³ indicate a weak paramagnetism of I at room temperature ($\mu_{\text{found}} = \sim 0.8$ B.M.). The bis-piperidine adduct or the solutions of I in pyridine are more strongly paramagnetic with moments of 1.9 ± 0.1 and 2.5 ± 0.2 B.M., respectively. The magnetic properties of I thus are consistent with those frequently observed for square planar Ni(II) complexes. However, the particular nature of the ligands in I forces us to assume that two electrons must be placed into a low-lying unoccupied molecular orbital of the complex as I would otherwise have to be formulated as a Ni(0) complex. I is also isolated in yields up to 14% per run if Ni(CO)₄ or finely divided metallic nickel is refluxed with a solution of diphenylacetylene and sulfur in toluene. This mode of preparation of I implies that the intermediate formation of a highly reactive, possibly free-radical-type, nickel sulfide (NiS₄³) may be responsible for this unusual reaction. A similarly reactive nickel sulfide may also be present as an "impurity" at the surface of the sulfur-rich nickelous sulfide used in the initial experiments. We are currently investigating the full scope of this reaction.

(3) The magnetic measurements were performed by H. M6dl, Technische Hochschule at Munich.

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RECEIVED JUNE 2, 1962

THE RELATIVE STRENGTHS OF ALKYL HALIDES AS PROTON ACCEPTOR GROUPS IN HYDROGEN BONDING¹

Sir:

In 1959 data were published on the shifts in frequency of the O-H stretching absorption bands of phenol and methanol upon hydrogen bond formation to alkyl halides.² The frequency shifts, $\Delta\nu$, increased as the halogen atom was changed in the order F < Cl < Br < I (Table I, column 2).³ By application of the Badger-Bauer rule⁵ relating

(1) Acknowledgment of partial support of this research is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (R.W.) and to the National Science Foundation (P.S.).

(2) P. von R. Schleyer and R. West, *J. Am. Chem. Soc.*, **81**, 3164 (1959). Also see M.-L. Josien, *et al.*, *Bull. soc. chim. France*, 423 (1957); **188** (1958); G. J. Korinek and W. G. Schneider, *Can. J. Chem.*, **35**, 1157 (1957).

(3) The same order of basicity holds for charge-transfer interactions of alkyl halides with halogens.⁴

(4) R. West, D. L. Powell, L. S. Whatley and M. K. T. Lee, unpublished data.

(5) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937); R. M. Badger, *ibid.*, **8**, 288 (1940); ref. 7, pp. 82-84.

spectral shifts and enthalpies of hydrogen bonds, our evidence was taken to indicate that proton acceptor ability of covalently-bound halogen atoms increased in the same sequence. This order has been used by others in discussing the relative basicity of alkyl halides toward protons⁶ and it therefore seems important to set forth our present modified views.

The recent accumulation of reliable thermochemical data on the strength of hydrogen bonds has made apparent the invalidity of the Badger-Bauer rule when applied to more than a limited series of closely related compounds.^{4,7,8} This evidence has led us to determine the thermodynamic properties of the interaction of phenol with alkyl halides; the results (Table I) quite contradict the earlier conclusion concerning the order of hydrogen bond forming ability of covalently bound halogens.⁹ Both the free energy and enthalpy of interaction tend to decrease in the order $F > Cl > Br > I$, the reverse of the spectral shift order. Baker and Kaeding¹⁰ have shown that the free energies of intramolecular hydrogen bonding between hydroxyl groups and halogens in 2,6-dihalophenols increase in the order $I < F < Br < Cl$; however, steric factors are expected to influence the free energy of interaction in these compounds.

TABLE I

THERMODYNAMIC PROPERTIES AND SPECTRAL SHIFTS OF HYDROGEN BONDS OF PHENOL TO ALKYL HALIDES AND ALKYL CHALCOGENIDES IN CCl_4 SOLUTION^a

Compound	$\Delta\nu$, cm. ⁻¹ ^b	$-\Delta H^0$, kcal./ mole	$-\Delta F^0$, 25°, kcal./ mole	$-\Delta S^0$, 25°, cal./deg. mole
Cyclohexyl fluoride	53	3.13	1.31	6.1
Cyclohexyl chloride	66	2.21	0.87	4.5
Cyclohexyl bromide	82	2.05	0.85	4.0
Cyclohexyl iodide	86	1.72	0.82	3.0
<i>n</i> -Butyl ether	278°	5.98	2.45	11.8
<i>n</i> -Butyl sulfide	254°	4.26	1.59	9.0
<i>n</i> -Butyl selenide	240°	3.72	1.46	7.6

^a Thermodynamic properties determined in the near infrared. See D. L. Powell, Ph.D. Thesis, University of Wisconsin, 1962, for the method of calculation. ^b Taken from ref. 2, or the present work, unless noted. ^c P. von R. Schleyer and L. Robinson, Abstracts, Fourth Delaware Valley Regional Meeting, Am. Chem. Soc., Philadelphia, Pa., Jan., 1962, p. 76. The corresponding spectral shift for phenol-*n*-butyl telluride is 220 cm.⁻¹.

In the previous communication,² it was also concluded that alkyl halides were relatively weak proton acceptors in hydrogen bonding. This conclusion is unchanged by the thermodynamic data, which show that such hydrogen bonds are quite weak compared with those from phenol to oxygen

(6) S. Andreades and D. C. England, *J. Am. Chem. Soc.*, **83**, 4670 (1961); J. R. Gersien, *J. Org. Chem.*, **26**, 758 (1961). Cf. J. E. Gordon, *J. Org. Chem.*, **26**, 738 (1961).

(7) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, 1960, pp. 82-85 and 348 ff.

(8) E. D. Becker, *Spect. Acta*, **17**, 436 (1961); H. Dunken and H. Fritsche, *Zeit. Chem.*, **1**, 127, 249 (1961).

(9) Added in proof: some measurements similar to those reported here have recently been presented in preliminary form, M.-L. Josien, *Pure Appl. Chem.*, **4**, 33 (1962).

(10) A. W. Baker and W. W. Kaeding, *J. Am. Chem. Soc.*, **81**, 5904 (1959); also see J. H. Richards and S. Walker, *Trans. Faraday Soc.*, **57**, 412 (1961).

or nitrogen bases (ca. 5-8 kcal/mole).^{4,7,8} Table I includes data for the enthalpy of hydrogen bonding of phenol to the di-*n*-butyl derivatives of oxygen, sulfur and selenium; a decrease in $-\Delta H^0$ in the order given was found. The trend thus parallels that found for the alkyl halides, but it is to be noted that both sulfur and selenium are capable of forming hydrogen bonds of appreciable strength, a fact not fully recognized heretofore.

The phenomenon of hydrogen bonding is not sufficiently understood at present to explain the data of Table I. However, it is not hard to understand in qualitative terms why $\Delta\nu$ and $-\Delta H^0$ should not correlate.¹¹ $-\Delta H^0$ measures the total energy of the interaction A-H...B-Y, *i.e.*, the strength of the H...B bond partially compensated by the weakening of the A-H and the B-Y bonds; $\Delta\nu$ measures the weakening of the A-H bond only. If the proton donor, A-H, is kept the same, $\Delta\nu$ and $-\Delta H^0$ may correlate for minor structural changes in the proton acceptor, *e.g.*, in Y, but not necessarily for major changes, *e.g.*, in the acceptor atom, B.

(11) We are indebted to Dr. H. J. Bernstein, National Research Council, Ottawa, for this observation. Dr. Bernstein (private communication) has demonstrated a simple relationship between $\Delta\nu/\Delta H^0$ for a given acceptor and the ionization potential for acceptor atoms in related molecules.

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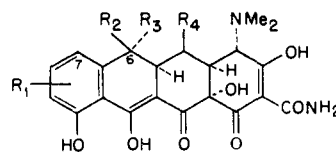
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RECEIVED MAY 31, 1962

THE TOTAL SYNTHESIS OF 6-DEMETHYL-6-DEOXYTETRACYCLINE

Sir:

The molecular structures of oxytetracycline (Ia) and chlorotetracycline (Ib) were elucidated in our laboratories a decade ago.¹ Since that



I

Ia Ib Ic

R ₁	H	Cl (7)	H
R ₂	OH	OH	H
R ₃	Me	Me	H
R ₄	OH	H	H

time, the tetracycline antibiotics have emerged as a unique class, whose characteristic chemotherapeutic activity is strictly dependent upon the main-

(1) (a) F. A. Hochstein, C. R. Stephens, L. H. Conover, P. P. Regna, R. Pasternack, K. J. Brunings and R. B. Woodward, *J. Am. Chem. Soc.*, **74**, 3708 (1952); F. A. Hochstein, C. R. Stephens, L. H. Conover, P. P. Regna, R. Pasternack, P. N. Gordon, F. J. Pilgrim, K. J. Brunings and R. B. Woodward, *ibid.*, **75**, 5455 (1953). Cf. also S. Hirokawa, Y. Okaya, F. M. Lovell and R. Pepinsky, *Z. Krist.*, **112**, 439 (1959). (b) C. R. Stephens, L. H. Conover, F. A. Hochstein, P. P. Regna, F. J. Pilgrim, K. J. Brunings and R. B. Woodward, *J. Am. Chem. Soc.*, **74**, 4976 (1952); C. R. Stephens, L. H. Conover, R. Pasternack, F. A. Hochstein, W. T. Moreland, P. P. Regna, F. J. Pilgrim, K. J. Brunings and R. B. Woodward, *ibid.*, **76**, 3568 (1954).