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 interelectronic 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 CH_2 and NH, respectively (J. Higuchi, private communication).

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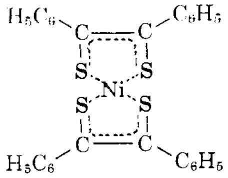
REACTION OF DIPHENYLACETYLENE WITH NICKEL SULFIDES

Sir:

The hypothesis that W. Steinkopf's well-known synthesis of thiophene from acetylene and pyrite[1] 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 $NiC_{28}H_{20}S_4$ (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 proton magnetic resonance spectrum of I in CS_2 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 measurements[3] indicate a weak paramagnetism of I at room temperature (μ_{found} = ~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 (NiS_4 ?) 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.

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

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

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

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THE RELATIVE STRENGTHS OF ALKYL HALIDES AS PROTON ACCEPTOR GROUPS IN HYDROGEN BONDING[1]

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 rule[5] 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.