ration of the two peaks (2.2 gauss) and about the same over-all width (3.7 gauss).

We should like to call attention to the similarities between these novel oxidation reactions of organophosphorus compounds and the observations of Kainer, Bijl, Rose-Innes, and coworkers[4] involving the complex of *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine with chloranil. These authors[4] have described magnetic susceptibility, molar conductivity, and ultraviolet and infrared absorption measurements on this type of complex which they call "an ionic magnetically decompensated molecular compound." It would appear that all of these phenomena might be included in the category of "charge-transfer complexes."[5] On this basis, the species responsible for the color and for the electronic paramagnetism in the reaction of the organophosphorus compounds could perhaps be described in terms of the *ground state* $(\overset{-}{A}\text{–}\overset{+}{D})$ or the corresponding radical ion pair (III, IV) and of the *excited state* (A, D), where A and D stand for the electron acceptor and donor, respectively. In the more usual charge transfer complexes,[5] the situation is reversed and the color is due to the transition $(A, D) \rightarrow (\overset{-}{A}\text{–}\overset{+}{D})$. More information is being sought in a detailed spectrophotometric study now in progress.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK

FAUSTO RAMIREZ
SAMUEL DERSHOWITZ

Received April 24, 1957

---

[4] H. Kainer and A. Überle, *Chem. Ber.*, **88**, 1147 (1955); H. Kainer and W. Otting, *Chem. Ber.*, **88**, 1921 (1955); H. Kainer, D. Bijl, and A. C. Rose-Innes, *Naturwissenschaften*, **41**, 303 (1954).

[5] (a) R. S. Mulliken, *Rec. trav. chim.*, **75**, 845 (1956) and references therein; (b) *cf.*, J. E. Wertz, *Chem. Revs.*, **55**, 922 (1955). We are grateful to Prof. Mulliken and Dr. Murrell (University of Chicago) for valuable theoretical suggestions.

The Direct *C*-Acylation of Pyridine

Sir:

We have succeeded in preparing pyridyl ketones by the reaction of pyridine and acid derivatives with amalgamated magnesium in 30–60% yields. Since the Friedel-Crafts and related reactions fail in the pyridine series, this new synthesis provides a means for obtaining directly a series of heterocyclic ketones heretofore available only through syntheses involving two or more steps.

The preparation of 2- and 4-benzoylpyridines was accomplished as follows: Magnesium, 24.3 g. (1.0 mole), was heated at 100° for 1 hr. with mercuric chloride, 46.0 g. (0.17 mole). The product (0.83 mole magnesium) was placed in a three-necked flask fitted with a stirrer, a reflux condenser, and a dropping funnel. A mixture of 25 g. each of pyridine and *N*,*N*-dimethylbenzamide was added and the materials heated to reflux. Within a few minutes a deep brown color appeared. The remainder of the pyridine, 250 g. (total 3.5 moles) was added slowly within 1 hr. Then the remainder of the amide, 273 g. (total 2.0 moles), was added over a period of 4 hr. maintaining the mixture at reflux throughout this period and until the magnesium disappeared (about 4 more hr.). The cooled reaction mixture was hydrolyzed with 100 g. of ammonium chloride in 500 cc. of water, filtered through Celite to remove insoluble salts, the upper layer of the filtrate extracted 5 times with 300-cc. portions of 6*N* HCl, the acid extracts made basic with 6*N* NaOH, the separated oil extracted with several 500-cc. portions of ether, the ether extracts dried and fractionally distilled, eventually under diminished pressure. The fraction b.p. 138–156° (2.8 mm.) was seeded with a crystal of 4-benzoylpyridine and was refrigerated in an ice box until no further product precipitated. Recrystallization of the solid from petroleum ether (90–100°) gave 8.2 g. (5.4% yield) of 4-benzoylpyridine, m.p. 72–73° (literature[1] 71.5–72.5°). The residual oil was redistilled and yielded 75.1 g. (50% theory) of 2-benzoylpyridine, b.p. 128–135° (1.0 mm.), literature[2] 133° (2 mm.). Total yield of benzoylpyridines based on gram atoms of magnesium reacted, 55.4%. A number of derivatives of each of the two isomers were prepared and found to correspond in properties with published values.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, IND.

G. BRYANT BACHMAN
R. M. SCHISLA

Received May 23, 1957

---

[1] K. E. Crook and S. M. McElvain, *J. Am. Chem. Soc.*, **52**, 4006 (1930).

[2] E. H. Huntress and H. C. Walter, *J. Am. Chem. Soc.*, **70**, 3704 (1948).

Reaction of *N*-Nitrosodibenzylamines with Sodium Hydrosulfite. A New Reaction

Sir:

We wish to report the discovery of a new reaction. The powerful reducing action of sodium hydrosulfite ($Na_2S_2O_4$) toward C-nitro and C-nitroso groups in basic media has previously been reported.[1,2]

An attempt to reduce *N*-nitrosodibenzylamines to the corresponding 1,1-disubstituted hydrazines using sodium hydrosulfite at 60° in basic ethanolic

---

[1] C. T. Redemann and C. E. Redemann, *Org. Syntheses*, Coll. Vol. III, 69 (1955).

[2] J. B. Conant and B. B. Corson, *Org. Syntheses*, Coll. Vol. II, 33 (1943).