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.

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(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.

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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

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(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).

solution gave instead a theoretical nitrogen evolution and hydrocarbon products. From N-nitrosodibenzylamine (I), m.p. 60–61°,[3] there was obtained a theoretical evolution of nitrogen and 77% of bibenzyl, m. p. 53-54°; a mixture melting point with an authentic sample of bibenzyl melted at 53.5–54.5°; with *cis*-1-nitroso-2,6-diphenylpiperidine (II),[4] m.p. 67–69°, 56.8% of *cis*-1,2-diphenylcyclopentane,[5] m.p. 43.5–45.5°, 21.4% of 1,5-diphenyl-1-pentene and a theoretical evolution of nitrogen was obtained. A 2,4-dinitrobenzenesulfenyl chloride derivative of the 1,5-diphenyl-1-pentene melted at 113–115°, (113.5–115°),[4] mixture melting point with the 2,4-dinitrobenzenesulfenyl chloride derivative of authentic[6] 1,5-diphenyl-1-pentene undepressed. An infrared spectrum of the mixture of products was identical with a mixture of authentic 1,5-diphenyl-1-pentene and authentic[7] *cis*-1,2-diphenylcyclopentane, m.p. 46–47°.

Treatment of *trans*-1-nitroso-2,6-diphenylpiperidine (III),[4] m.p. 87–89.5°, with sodium hydrosulfite gave a 60.4% of a mixture of *trans*-1,2-diphenylcyclopentane and *cis*-1,2-diphenylcyclopentane, 19% of 1,5-diphenyl-1-pentene and a theoretical nitrogen evolution. The infrared spectrum of the mixture of products was identical with that of a mixture of authentic *cis*- and *trans*-1,2-diphenylcyclopentane, and 1,5-diphenyl-1-pentene.

Reaction of N-nitrosobenzylphenylamine (IV) with sodium hydrosulfite yielded no nitrogen but gave instead a 77% yield of 1-benzyl-1-phenylhydrazine, hydrochloric acid salt, m.p. 170–172° (m.p. 167–170°).[8] With N-nitrosodiphenylamine (V) an 80% yield of diphenylamine, m.p. 53.2–54.4°, (m.p. 53.9°)[8] was obtained, sulfuric acid salt, m.p. 124.5–126° (123–125°).[9] The formation of diphenylamine on reduction of V has previously been reported using other reducing agents.[10] Treatment of *cis*-1-nitroso-2,6-dimethylpiperidine[3] (VI) yielded *cis*-1-amino-2,6-dimethylpiperidine, picrate salt, m.p. 167.5–169° (m.p. 168–169),[3] a mixture with the picrate of authentic *cis*-1-amino-2,6-dimethylpiperidine, m.p. 167–168°, melted at 167–169°

The products of the reaction of I, II, and III with sodium hydrosulfite are identical with those isolated in the mercuric oxide oxidation of the corresponding 1,1-disubstituted hydrazines,[4] suggesting a common intermediate for both reactions. Further work on the reaction of sodium hydrosulfite with N-nitrosodialkylamines is presently under investigation and will be reported at a later date.

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Free-Radical Methylation of Simple Aromatic Hydrocarbons

Sir:

The free radical methylation of anthracenes,[1] trinitrotoluene,[2] and pyridines[3] has been reported[4a]. However, there appears to be no record[5] of substitution of methyl radicals on simple aromatics not activated by electron-withdrawing substituents; in fact, it has been suggested that such a reaction is energetically disfavored.[6]

We now wish to report that heating a *ca.* 1M solution of acetyl peroxide in toluene at the boiling point gives (in addition to bibenzyl and other dimeric or polymeric material) *o*-, *m*-, and *p*-xylene as well as ethylbenzene and an unidentified C_9 aromatic hydrocarbon fraction, the latter in very small amount. The over-all yield of C_8 aromatics isolated by careful fractional distillation is *ca.* 10% based on acetyl peroxide. The composition of this fraction, as determined by gas chromatography and ultraviolet analysis, is *o*-xylene, 44.5%, *m*-xylene, 21%, *p*-xylene, 13.5%, and ethylbenzene, 21%. Moreover, the reaction of benzene with acetyl peroxide yields (besides higher-boiling products[4b]) toluene, identified by boiling point, infrared spec-

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(5) M. S. Kharasch, A. Fono, and W. Nudenberg [*J. Org. Chem.*, **16**, 111 (1951)] have stated that the decomposition of acetyl peroxide in benzene yields toluene and xylenes, but no experimental data are available.

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