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derived by the usual formulae. One hundred and three reflections were recorded. In space group $P2_1/a$ there is one molecule in the asymmetric crystal unit, and the orientation of this molecule in the unit cell was deduced by Fourier-transform methods and from the intramolecular peaks in the Patterson projection. However, it was impossible to pack molecules in this orientation into the unit cell in space group $P2_1/a$, so that it seemed that there might be two molecules in the asymmetric unit arranged in space group Pa, the 010 and 030 reflections being by chance too weak to be observed, and the $N(z)$ test being misleading (a not uncommon occurrence). Alternatively there might be some type of disordered arrangement of molecules. The problem, therefore, seemed too complex for solution by the usual trial and error methods, and no further detailed structural analysis is proposed. The structure-factor data have been recorded (3).

We thank the National Research Council for financial support.

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RECEIVED JUNE 12, 1961.
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A NEW METHOD FOR THE DEOXYGENATION OF AROMATIC *N*-OXIDES

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In the course of a study of the cyclization of some nitrophenylpyridine derivatives with ferrous oxalate it was observed that when 2-*o*-nitrophenylpyridine-*N*-oxide was heated with this reagent the only product isolated was pyrido[1,2-*b*]indazole (1). It was also shown that the first stage in this reaction was probably the elimination of the *N*-oxide grouping; 2-phenylpyridine-*N*-oxide itself was deoxygenated under these conditions but was unaffected in the absence of the ferrous oxalate.

The scope of this deoxygenation has now been extended to a number of other pyridine-*N*-oxide derivatives and to *N*,*N*-dimethylaniline-*N*-oxide. The results are summarized in the table.

N-Oxide	Yield of tertiary amine, %
Pyridine-*N*-oxide	64
2-Picoline-*N*-oxide	62
3-Picoline-*N*-oxide	72
2-Aminopyridine-*N*-oxide	45
2-Phenylpyridine-*N*-oxide	63
N,*N*-Dimethylaniline-*N*-oxide	55 (crude)

This new procedure may well be of value, particularly in cases (e.g. when an amino group is present) where other methods currently in use (such as that involving phosphorus trichloride) may not be employed. Its limitations include applications to (*a*) those substances containing groupings, e.g. nitro, which are attacked by ferrous oxalate; and (*b*)

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probably aliphatic tertiary amine *N*-oxides, which are known (see ref. 2) to undergo elimination of the amine group by the action of heat and to give an olefin.

EXPERIMENTAL

The *N*-oxide was mixed with 4 molar equivalents of ferrous oxalate dihydrate and granulated lead (ca. 6 g/g of *N*-oxide), and the mixture ((*a*) in a flask arranged for distillation for *N*-oxides of liquid amines, or (*b*) in a flask fitted with a condenser for *N*-oxides of solid amines) was heated in a metal bath at 300° (bath temperature) for 30 minutes. The product isolated by distillation (in case (*a*)), or by ether extraction of the reaction mixture (in case (*b*)), was dried overnight over potassium hydroxide pellets. The identity of the products was established by comparison of their infrared spectra with those of authentic samples of the bases. The picrates of the products were prepared in the cases of pyridine-, 2-picoline-, 3-picoline-, and 2-phenylpyridine-*N*-oxides, and their identity confirmed by melting point and mixed melting point determinations. 2-Aminopyridine, as isolated from this reaction, was recrystallized from light petroleum (40–60°) and had m.p. 57–59°, which was not depressed on admixture with an authentic sample.

ACKNOWLEDGMENTS

This work was carried out during the tenure (by K. A. H. A.) of a C.I.L. Fellowship, and with the financial support of the National Research Council.

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Received July 3, 1961.
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THE IRRADIATION OF β-IONONE

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Study of the literature suggests that the irradiation of substances containing the system (I) where Y is carbon and (or) a hetero atom(s) leads to (reversible) hydrogen transfer and the formation of (II) which may then be further transformed. In those cases noted there is the possibility of $n \rightarrow \pi^*$ excitation, though this may not be a requirement. The irradiation of α,β-unsaturated ketones ((I), Y = $C \cdot CH_3$) gives, for example, the β,γ-unsaturated isomer (1). All the requirements of the *o*-nitrobenzaldehyde ((I), Y = NO) – *o*-nitrosobenzoic acid conversion and related changes are met by the postulation of an intermediate ketene formed by hydrogen transfer (2). Recently it has been shown that substituted benzophenones ((I), Y = $C \cdot Ph$) are enolized by irradiation (3).

β-Ionone (III) on irradiation has been shown (4) to give (reversibly) the pyran (IV) as main product, together with a by-product which was tentatively attributed the structure (V). The alternative (VI) was considered and rejected on reasonable but negative evidence. Since β-ionone falls into the class of substance under present consideration, by vinylogous extension, (VI) seemed mechanistically much more favored. We have repeated the preparation and determined the n.m.r. spectrum (Fig. 1), which was not available at the time of the earlier work.