SUMMARY.

The photochemical properties of the pyridine nucleus were investigated using the 3,5-dicarboalkoxy-pyridine system as a model. Photochemically induced reduction to dihydropyridines (DHP's) was anticipated as an important reaction and the carboalkoxygroups were expected to stabilize the reduction products. To stimulate possible valence bond isomerisation a considerable degree of overcrowding around the ring was effected by substituting the remaining 2-, 4- and 6-ring positions with alkyl groups.

In actual fact the parent compound, 3,5-dicarbomethoxy-pyridine, showed on irradiation in alcoholic or hydrocarbon solvents as the only observable process reduction of the pyridine nucleus. As products were formed mainly 2-alkyl-1,2- and 4-alkyl-1,4-DHP's originating by the addition of a solvent molecule to the aromatic ring, as well as 1,2- and 1,4-DHP's formed by the take-up of one mol. of hydrogen. In isopropanol 1,2-DHP dimers were formed (ch. 2.4.1.). A similar picture with some variation in the product distribution was observed with 2,6-dimethyl-3,5-dicarboalkoxy-pyridine. In this case by using ethanol or isopropanol as the hydrogen source the major product was the 1,4-reduced form of the starting material. Experiments with O-D labelled alcohols confirmed that exclusively the hydroxyl hydrogen becomes incorporated in the 4-ring position.

On the basis of the product pattern, the above mentioned labelling experiments, the quantum yields, and other observations a mechanism is proposed in which the DHP's originate from initial hydrogen abstraction of the solvent (alcohols) by the nitrogen center of an excited pyridine species, followed by either radical coupling of DHP radicals to dimers, or radical disproportionation to reduced starting material (ch. 6.2.).

Irradiation of 2,4,6-trimethyl-3,5-dicarboalkoxy-pyridine gave besides DHP formation also ring contraction to 2,4,5-trimethyl-3-carboalkoxy-pyrrole. The ring contraction was likely not attended with a scrambling of the remaining skeletal atoms as confirmed by using pyridine labelled with deuterium
in the 4-methyl group; this group appeared in the 4-position of the pyrrole. In view of this result the pyrrole is thought to originate by hydrogen abstraction by the pyridine nitrogen with subsequent extrusion of carboalkoxy carbene, which results in bond formation between the 2- and 4-pyridine skeletal atoms (see ch. 6.2.).

Unlike the thus far mentioned pyridines an efficient valence isomerisation was observed as the exclusive process with the more crowded 2,6-dimethyl-4-isopropyl-3,5-dicarboethoxypyridine. Irradiation in cyclohexane yielded three isomers: 5,6-dimethyl-2-isopropyl-3,4-dicarboethoxypyridine, 3,6-dimethyl-5-isopropyl-2,4-dicarboethoxypyridine and 4,6-dimethyl-3-isopropyl-2,5-dicarboethoxypyridine (see ch. 2.4.4.). The structure of the former isomer was established by a separate synthesis, whereas the other two structures were assigned on the spectral and chemical properties of the compounds. When methanol instead of cyclohexane was used as the solvent, the 3,4-dicarboalkoxy pyridine was the only isolable photoproduct.

For these isomerisations a mechanism is considered invoking 1,4- and 2,5-bridged dewar pyridines and their derived prismanes, the rearrangements of which give only the observed photoisomers (ch. 6.3.).

In contrast to the free bases the related N-methyl pyridinium salts and the carbon analogue, dimethyl isophthalate, appeared to be (almost) photostable. The pyridinium salts displayed unlike the free bases photoenolisation involving the ester carbonyl and the ortho methyl groups (ch. 3.).

Considerable attention was paid to the multiplicity and electronic configuration ($\pi-\pi^*$ or $n-\pi^*$) of the excited species causing photoreduction. In this connection an $n-\pi^*$ singlet (92.5 kcal/mol) was observed from the absorption spectrum, and a singlet (ca. 89 kcal/mol) and triplet (ca. 73 kcal/mol) both of $\pi-\pi^*$ nature were detected (ch. 4.). The fluorescence was observed to be quenched by several potential hydrogen donors, for which a relation of quenching rates and the C-H bond energy is suggested.

The photoreduction appeared to be initiated by a singlet excited state as confirmed by a kinetic correlation of fluorescence quenching and photoreduction rates and the absence of any inhibition of the reduction by triplet quenchers.
(ch. 5.). Although the fluorescence quenching of a \( \pi-\pi^* \) singlet is affected, it is believed (ch. 6.2.) that an \( n-\pi^* \) singlet cannot \textit{a priori} be excluded as the actual reactant. In the case that a \( \pi-\pi^* \) singlet is responsible for the reduction an excited "pre-dewar" pyridine with radical character on nitrogen is suggested to cause, dependent on the system, either hydrogen abstraction or valence isomerisation.