A New Synthetic Method for the Preparation of Aromatic Aldehydes, Ketones, and Schiff Bases

By JOHN C. LEFFINGWELL* and H. J. BLUHM

(*Research and Product Development Departments, R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina* 27102)

Summary Activated manganese dioxide oxidatively dehydrogenates certain cyclohexene aldehydes, ketones, and Schiff bases to the corresponding aromatic derivatives.

THE discovery by Ball, Goodwin, and Morton[1] in 1948 that manganese dioxide effected dehydrogenation of vitamin A alcohol into vitamin A aldehyde in neutral media led to a series of investigations on the oxidizing ability of manganese dioxide[2] to produce $\alpha\beta$-unsaturated ketones and aldehydes. However, reports of aromatizations using MnO_2 are few[3-5] and no reports have appeared on the oxidative dehydrogenative aromatization of simple cyclohexene systems to the corresponding benzenoid systems with manganese dioxide.

We report that an excess of activated manganese dioxide† oxidatively dehydrogenates certain cyclohexene aldehydes, ketones, and Schiff bases to the corresponding aromatic derivatives. The reactions were carried out either in refluxing benzene or hexane under anaerobic conditions; yields reported are of highly purified distilled materials.

Thus, aromatic aldehydes and ketones are now readily available through the general procedure described above

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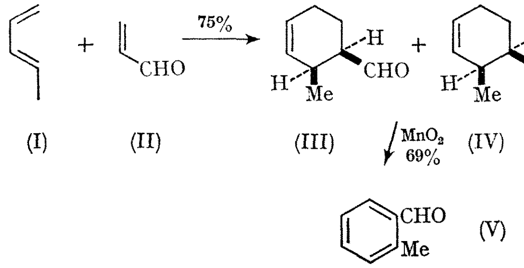
† In addition, nickel peroxide and lead dioxide were found to produce similar transformations, but in lower yields.

for the oxidative aromatization of substituted cyclohexenes derived from the Diels–Alder reaction of $\alpha\beta$-unsaturated carbonyl compounds and 1,3-diolefins.

TABLE

Starting material	Solvent	Products	Yield (%)
Cyclohexene-3-carbaldehyde	Benzene	Benzaldehyde	55
2-Methylcyclohexene-4-carbaldehydes‡	Benzene	*o*-Tolualdehyde	60
2-Methylcyclohexene-3-carbaldehydes‡	Benzene	*o*-Tolualdehyde	69
2,6-Dimethylcyclohexene-3-carbaldehydes‡	Benzene	2,6-Dimethylbenzaldehyde	36
4-Acetylcyclohexene	Benzene	Acetophenone	71
N-(3-Cyclohexenylmethylidene)isobutylamine	Hexane	*N*-Benzylideneisobutylamine	3

In the thermal Diels–Alder reactions employed for preparing the starting aldehydes and ketones[6] for our study, it was observed (in some cases) that several isomeric products were formed. For example, thermal condensation of commercial penta-1,3-diene (I) with acraldehyde (II) afforded a ratio of 78% *cis*- (III) and 18% *trans*-2-methylcyclohexene-3-carbaldehyde (IV). These two components were conveniently separated by fractional distillation for experiments designed to determine which isomer would favour dehydrogenation. Although a slight kinetic preference for aromatization of the *cis*-isomer (III) was noted, any accurate observation as to the relative rates was precluded by the partial equilibration of the *cis*/*trans*-isomers during the course of the reaction even in nonpolar solvents (hexane, *etc.*). A careful rate study to determine the relative dehydrogenation preference for the configurational isomers would be useful for clarifying the mechanism of the metal oxide hydrogen abstraction, that is, whether the mechanism is a concerted *cis*-2H abstraction or a non-concerted radical abstraction.



Results to date on extending the generality of this reaction to cyclohexene esters, such as methyl 2-methylcyclohexene-3-carboxylate, have been negative.

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‡ A mixture of *cis*/*trans*-isomers was employed.

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