dimethyl-7-isopropylazulene. The position of the carboxyl group which formed the lactone ring in carpesia lactone was determined.

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78. Shigehiko Sugasawa and Kitaro Mizukami: Application of the Ball Reaction on Aromatic Alcohols. I.

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According to Ball, Goodwin, and Morton,[1] polyene alcohols can advantageously be converted into the corresponding unsaturated aldehydes by means of active manganese dioxide in indifferent solvent such as petroleum ether and they succeeded in preparing vitamin A aldehyde from vitamin A. Later, Attenburrow[2] has shown that Ball's elegant method can be applied to α,β-monounsaturated alcohol, allyl alcohol being oxidized to acroleine, and Sondheimer[3] was the first to introduce this method into the field of steroid chemistry.

We are now reporting that Ball's method is also applicable to aromatic alcohols, yielding the corresponding aldehydes in good or fair yield under very mild working conditions. Our result is, therefore, at variance with that of Ball *et al.*, who reported their unsuccessful attempt to oxidize benzyl alcohol to benzaldehyde. In our case this oxidation proceeded quite smoothly at ordinary temperature, giving benzaldehyde in a good yield, when benzyl alcohol dissolved in ether was mixed with active manganese dioxide, a slight evolution of heat being observed. We cannot guess the reason for their failure but it may depend upon the activity of the manganese dioxide used, which was prepared according to Attenburrow in the present experiments.

As is shown in Table I, this method is applicable not only to isocyclic aromatic alcohols, but also to some of heterocyclic alcohols.

Table. I.[f]

Aldehyde	React. temp.	Time (hr.)	Yield[c] of semicarbazone (%)
Benz-	Room temp. (22°)	2	70 (215~216)[d]
Veratr-	35°	1	65 (177)
Salicyl-	Room temp. (20°)	3	60 (224)
Furfur-	Room temp. (19~20°)	3.5	40 (190~192)
3-Pyridyl-[a]	Room temp. (21°)	1.5	50 (213~214)
4-Pyridyl-[b]	35°	3	60 (213~215)[e]

a) This aldehyde is not readily soluble in ether, so $CHCl_3$ was used as a solvent.
b) Ether added with 5% EtOH was used as a solvent.
c) The yield is based upon semicarbazone once crystallized from a suitable solvent.
d) Figures in parentheses show melting or decomposition point of the semicarbazone.
e) Thiosemicarbazone, m.p. 219~221°(decomp.).
f) This table shows the result of only one experiment for each compound and no special effort was made to find out working conditions for optimal yield. The solvent used was ether unless otherwise stated.

Experiments with alcohols having other functional groups, such as nitro, hydroxyl, etc. and with polyhydric alcohols are now under progress and their results will be published in the forthcoming paper.

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1) Ball, Goodwin, Morton: Biochem. J., **42**, 516(1948).
2) Attenburrow: J. Chem. Soc., **1952**, 1094.
3) Sondheimer: J. Am. Chem. Soc., **75**, 5930(1953).

Experimental

General Procedure—The alcohol (0.5~1.0 g.) was dissolved in about 10 volumes of ether (50~100 cc.) and to this was added dried active MnO_2.[4] The whole was stirred for 1~3 hrs. at temp. ranging from 20° to 35°, during which time the original chocolate colored MnO_2 changed to dark brown. Then this was filtered, washed with ether, and the solvent was evaporated from the combined ethereal solution leaving the crude aldehyde. The semicarbazone was prepared as usual and purified from a suitable solvent and was identified with the authentic specimen by direct comparison.

Summary

The oxidation method of Ball, Goodwin, and Morton for polyene alcohols to the corresponding aldehydes, using active MnO_2 in an indifferent solvent, was proved to give satisfactory results when applied on aromatic alcohols, isocyclic and some heterocyclic as well. Manganese dioxide prepared according to Attenburrow was recommended for this purpose.

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4) This was prepared according to Attenburrow and about ten times in weight of the starting alcohol was used. In one experiment, where three times MnO_2 was used the result was not satisfactory.