

## REDUCTION BY DISSOLVING METALS

### XIX.\* A SYNTHESIS OF 4-ISOPROPYLCYCLOHEXA-1,4-DIENECARBALDEHYDE

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#### Abstract

A method of protecting benzaldehyde carbonyl groups during metal-ammonia reductions by intermediate conversion into the *N,N'*-dimethylimidazolidine by reaction with *N,N'*-dimethylethylenediamine, has been exemplified by conversion of 4-isopropylbenzaldehyde into its 2,5-dihydro derivative. This is a principal flavouring matter of cumín seeds.

The isolation of 4-isopropylcyclohexa-1,4-dienecarbaldehyde (1) from extracted ground cumín seeds<sup>1</sup> represents the first observation of what is probably the precursor of the previously isolated 4-isopropylbenzaldehyde and phellandral. In view of the importance of cumín as a flavouring material in Eastern cookery, we have devised a practical synthesis; isolation of the pure compound from natural sources is difficult because of its tendency to disproportionation, isomerization, and oxidation even on examination by g.l.c. In fact the synthetic material has a genuine odour of fresh cumín, being stronger and sweeter than cuminaldehyde.

The synthesis of the aldehyde had previously been carried out<sup>2</sup> by Birch reduction of a protected cuminaldehyde derivative, but the aldehyde had not itself been examined, merely being characterized as the 2,4-dinitrophenylhydrazone. The present synthesis is different in detail, but uses the same principle, that hydrogenolysis of benzylic amines does not occur on Birch reduction, in contrast to most benzylic ethers.

Cuminaldehyde was synthesized from cumene by *p*-bromination, and the derived Grignard reagent was made to react with ethyl orthoformate.<sup>3</sup> Protection was readily accomplished by conversion into the imidazolidine derivative (2) which was reduced to the diene (3). Careful acid hydrolysis then produced the diene aldehyde (1). The properties of the synthetic compound agree with those reported.<sup>1</sup> The 2,4-dinitrophenylhydrazone was found to be sensitive to the method of preparation, and the m.p. (206–209°) is higher than that (199°) previously reported.<sup>2</sup>

\* Part XVIII, *J. chem. Soc. Perkin I*, 1972, 1546.

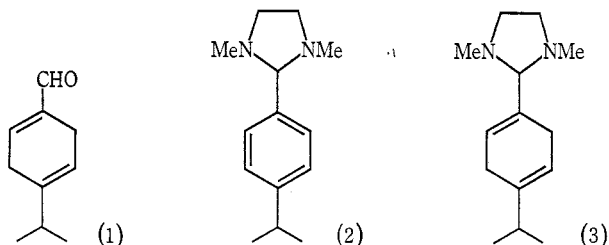
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<sup>1</sup> Varo, P. T., and Heinz, D. E., *J. agric. Fd Chem.*, 1970, **18**(2), 239.

<sup>2</sup> Birch, A. J., Cymerman-Craig, J., and Slayter, M., *Chemistry Ind.*, 1954, 1559.

<sup>3</sup> Bachman, G. B., *Org. Synth.*, 1943, Coll. Vol. II, 323.

The compound presumably results biogenetically from the selective oxidation of  $\gamma$ -terpinene, although this hydrocarbon has not been observed in the oil.



### Experimental

#### 4-Isopropylcyclohexa-1,4-dienecarbaldehyde (1)

Cumene was brominated<sup>4</sup> to 4-bromoisopropylbenzene, b.p. 46–49°/10.5 mm,  $t_R$  2 min (3% SE-30 at 140°). Only minor proportions of impurities were present from g.l.c. examination. 4-Isopropylbenzaldehyde was obtained by reaction of the Grignard reagent from the bromide with ethyl orthoformate by the general literature process.<sup>3</sup> An entrainment technique in the Grignard reaction gave good yields of product. The solution of 4-bromoisopropylbenzene (50 g, 0.251 mol) and methyl iodide (35.5 g, 0.251 mol) in ether (200 ml) was added slowly to react with magnesium (12.5 g, 0.51 mol) with stirring. After 2 hr under refluxing conditions ethyl orthoformate (75 g, 0.51 mol) was added over 15 min and the mixture heated under reflux for 15 hr. On working up in the usual way, with acidification, 4-isopropylbenzaldehyde (25 g, 67%) was obtained, b.p. 65–68°/1 mm,  $\nu_{\max}$  2720, 1690, 835  $\text{cm}^{-1}$ .

The aldehyde (25 g, 0.169 mol) in benzene (100 ml) was added slowly with stirring to *N,N'*-dimethylethylenediamine (13.5 g, 0.154 mol) in benzene (50 ml) and the mixture was maintained at 60° for 2 hr. The product, 1,3-dimethyl-2-(4'-isopropylphenyl)imidazolidine (22 g, 69%) and b.p. 100–105°/1 mm. G.l.c. showed absence of all but a trace of isopropylbenzaldehyde, with a major single peak  $t_R$  3.2 min (SE-30, 180°);  $\nu_{\max}$  2770 (NME) with no NH or C=O absorption;  $\delta$  1.3 (6H, d,  $J$  7 Hz); 2.2 (6H, s); 2.6 (2H, m); 2.9 (1H, m); 3.3 (1H, s); 3.4 (2H, m); 7.35 (4H, AB quartet).

The imidazolidine (5 g, 0.023 mol) in dry tetrahydrofuran (15 ml) and *t*-butyl alcohol (20 ml) was added to pure ammonia (250 ml) followed by lithium (2 g, 0.29 mol) and the mixture left under reflux with stirring for 2 hr. Addition of some methanol, evaporation of ammonia, cautious addition of water, and ether extraction gave the dihydroimidazolidine.

Reaction with 2*N* hydrochloric acid and extraction of the product, followed by distillation, gave 4-isopropylcyclohexa-1,4-dienecarbaldehyde, b.p. 70–71°/1 mm (2.5 g, 72%) (Found: C, 79.1; H, 9.4. Calc. for  $\text{C}_{10}\text{H}_{14}\text{O}$ : C, 79.8; H, 9.3%); the analysis was difficult because of the instability of the compound. G.l.c. with a major peak at  $t_R$  3.3 min (SE-30, 140°) showed additionally a trace of 4-isopropylbenzaldehyde. Spectra:  $\delta$  1.05 (6H, d,  $J$  6 Hz); 2.2 (1H, m); 2.9 (4H, b s); 5.58 (1H, b s); 6.9 (1H, b s); 9.57 (1H, s);  $\nu_{\max}$  2720, 1675, 1640, 1610sh, 800, 775  $\text{cm}^{-1}$ ;  $\lambda_{\max}$  (hexane) 212, 248 nm. The 2,4-dinitrophenylhydrazone had m.p. 206–209° (lit.<sup>2</sup> 199°).

<sup>4</sup> Qvist, W., *Chem. Abstr.*, 1937, **31**, 6627.