

thiothiophthene. One of us (A. H.) wishes to thank *The Norwegian Research Council for Science and the Humanities* for economic aid.

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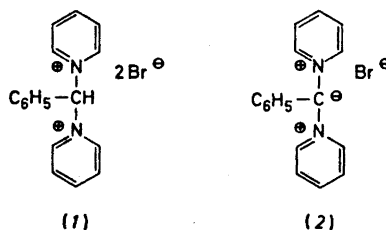
An Improved Method for the Preparation of 1-Deuterated Aldehydes

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Several methods exist for the preparation of 1-deuterated aldehydes.¹ However, these methods are usually inexpedient due to any of the following limitations: low

synthetic yields, low deuterium incorporation, costly reagents, inaccessibility of starting materials or limited applicability. Recently, a convenient method for the conversion of *gem*-dihalides into 1-deuterated aldehydes was described.² In this case, benzylidene dibromide was converted into the bisiminium salt (1) which was isolated and allowed to exchange a deuterium (from deuterium oxide) *via* the ylide (2). Warming of the reaction mixture then furnished benzaldehyde-*d* and pyridine in high yield and with high deuterium incorporation.



It has now been found that the *gem*-dibromides required can be generated *in situ* from the corresponding aldehydes and that the bisiminium salts need not be isolated. The preparation and purification of frequently unstable *gem*-dibromides is therefore unnecessary.

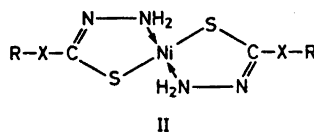
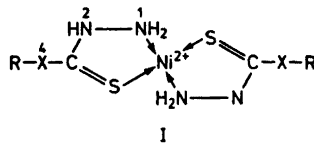
The procedure consists (method A) of the addition of 4 mmoles of the aldehyde to a stirred pre-prepared solution of triphenylphosphine dibromide in pyridine (from 8 mmoles of bromine and triphenylphosphine and 15 ml of dry pyridine). The resulting thick slurry is warmed for 2 h at 70°C, cooled to 0°C, and 10 ml of deuterium oxide is added. After standing overnight at room temperature, the clear solution is warmed for 30 min at 70°C, extracted with petroleum ether, washed repeatedly with water, and the aldehyde from the dried solution purified by column chromatography.

In this way, anisaldehyde is converted in 85 % yield into anisaldehyde-*d* of 90 % isotopical purity (by PMR). By repeating the procedure an isotopical purity of 99 % can be attained.

The bisiminium salt can be isolated by the addition of dry ether, filtration under nitrogen and washing with ether. The reaction (method B) of isolated anisaldehyde-derived bisiminium salt with buffered deuterium oxide according to the

original procedure¹ does not significantly improve the yield or isotopic purity. In the case of furfural a good deuterium incorporation (90%) but a very low yield (less than 10%) is obtained both by method A and B (extraction with ether).

As formaldehyde-*d*₂ was also prepared by the original method,² it appears that by the present modification aliphatic and aromatic 1-deuterated aldehydes can be conveniently prepared, as long as the undeuterated starting aldehyde is available.



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Cotton Effects of *d-d*-Transitions of Optically Active Nickel(II)-Complexes II

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In a previous publication¹ it was reported that compounds of the types I and II may exhibit circular dichroism in the region of the ligand field bands provided R is a carbon group containing an asymmetric carbon atom and X=NH.

No Cotton effect was observed when the asymmetric atom was not at the α -position of the R group (e.g. $-\text{CH}_3-\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$). The magnitude of the molar circular dichroism seemed very much to depend upon the asymmetric bulk of the group. For some complexes the effect was surprisingly large and it was suggested that an effective interaction, probably a specific solvation, transferred the asymmetry from the group to the metal chelate ring. This is a plausible proposition because the N^4 atom (X=NH) neighbour to the asymmetric carbon atom will itself be asymmetric and thus one of the diastereoisomers will be energetically more stable than the other. Hydrogen bonding from N^4 and N^3 to a solvent molecule (ethanol) may then induce asymmetry in the chelate ring so that the nickel $d \rightarrow d$ transitions become optically active.

In order to test this hypothesis we have prepared some analogous compounds in which X is CH_3 or O. When X= CH_3 no asymmetry can be connected with this group and further no asymmetry can be transferred since CH_3 cannot participate in hydrogen bonding. Therefore, it is in accordance with the described ideas that nickel(II) complexes of optically active β -phenylthiobutyrohydrazide, $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{CH}_2\text{CSNHNH}_2$, show no Cotton effect in the range of the visible absorption band.

When X=O (an *O*-alkyl thiocarbazate, or "xanthogenhydrazide") the O cannot be chiral by itself. However, it may participate in hydrogen bonding and thus become chiral and give rise to the formation of diastereoisomers in a ratio different from 1:1. This asymmetry may then be transferred to the chelate ring by hydrogen bonding. In agreement with this proposition it was found that the nickel complex of an optically active *O*-menthyl thio-