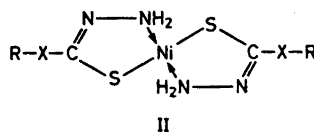
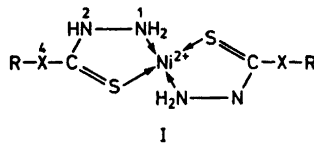


original procedure¹ does not significantly improve the yield or isotopic purity. In the case of furfural a good deuterium incorporation (90%) but a very low yield (less than 10%) is obtained both by method A and B (extraction with ether).

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

K. A. JENSEN, GUNNAR CEDERBERG,
R. B. JENSEN and ERIK LARSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark

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-

carbazate exhibited a significant Cotton effect.

In our previous publication we mentioned that there seemed to be a correlation between the absolute configuration * and the sign of the circular dichroism of the nickel transitions. This is not borne out by an investigation of a new thiosemicarbazide with $R=(S)$ -1-methyl-2-phenylethyl ("amphetamyl"). The sign of the circular dichroism band of the nickel complex of this thiosemicarbazide is opposite to that of the thiosemicarbazide complexes investigated earlier although the sequence of the groups arranged with respect to steric bulk viewed from N^4 is the same. Further experiments on this problem are in progress.

Experimental. Circular dichroism measurements were performed with a Roussel-Jouan Dichrograph. The absorption spectra were measured with a Cary Model 14 recording spectrophotometer and the optical rotations with a Perkin-Elmer polarimeter 141.

The rotations of the optically active compounds are given in Table 2. Melting points given below refer to racemic compounds IV-VI.

β -Phenylbutyric acid (III) was prepared according to the literature and resolved through its menthol ester.⁴ Optically active β -phenylbutyric acid was transformed into optically active β -phenylthiobutylhydrazide by the method of Jensen and Pedersen,^{5,6} i.e. via IV and V.

1-(β -Phenylthiobutyl)piperidine (IV). β -Phenylbutyl chloride (b.p. 112–114°C at 12 mmHg, prepared from the acid and thionyl chloride) was converted into the piperidide (b.p. 156–158°C at 1 mmHg) by reaction with piperidine in ether. The thiopiperidide was prepared in a similar manner to thiopropionylpiperidine,⁵ however, the residue obtained after evaporation of the ether extract was not distilled but recrystallized from light petrol. Yield 65%. M.p. 55–56°C. (Found: C 73.20; H 8.60; N 5.70. Calc. for $C_{15}H_{21}NS$: C 72.87; H 8.50; N 5.67).

S-Carboxymethyl- β -phenylthiobutylpiperidinium bromide (V). IV (10 g) and bromoacetic acid (6.1 g) were dissolved in dry benzene (100 ml). After standing for 24 h at room temperature a crystalline precipitate had formed. It was filtered off and washed with ether. Yield 13 g (84%). M.p. 150–151°C

* Concerning the absolute configuration of β -phenylbutyric acid and 1-methyl-2-phenylethylamine, see Refs. 2 and 3.

(Found: C 53.00; H 6.28; N 3.47; S 8.07. Calc. for $C_{17}H_{24}NO_2SBr$: C 52.84; H 6.22; N 3.63 S 8.29).

β -Phenylthiobutylhydrazide hydrochloride (VI). Following the method of Ref. 5 carboxymethyl β -phenylthiobutylhydrazide (2.1 g, from 5 g of V) was obtained as a reddish oil. This was not purified further but was dissolved in 16 ml 0.5 N NaOH whereafter 0.40 g of hydrazine hydrate was added while cooling in ice. The solution was adjusted to pH 6 by addition of hydrochloric acid and extracted with ether. The hydrochloride of the hydrazide was precipitated from the dried ether solution ($MgSO_4$) by addition of an ether solution of HCl. On removal of the ether *in vacuo* the solution left a yellowish oil which crystallized on standing in a refrigerator. After washing the crystals with dry ether and several times with pentane they became colourless. Yield 20%. M.p. 116–118°C. (Found: C 52.12; H 6.51; N 12.06. Calc. for $C_{16}H_{18}ClN_2S$: C 52.06; H 6.51; N 12.15). The inner complex nickel compound is reddish-brown. (Found: C 54.20; H 6.04; N 12.51. Calc. for $C_{20}H_{22}N_4NiS_2$: C 53.95; H 5.89; N 12.68). V formed with methylhydrazine a methyl hydrazide which was not isolated in the pure state; however, with nickel chloride it formed a reddish-brown, very slightly soluble ionic complex $(CH_3(CH_2(C_6H_4)CH_2CSN(CH_3)NH_2)_2NiCl_2$. (Found: C 48.10; H 5.87; N 10.13; S 11.60. Calc. for $C_{22}H_{32}Cl_2N_4NiS_2$: C 48.39; H 5.87; N 10.26; S 11.93).

O-Menthyl thiocarbazate hydrochloride (VII). Sodium *O*-menthyl dithiocarbonate (sodium menthyl xanthate) was prepared from natural (*R*)-menthol⁷ and transformed into *S*-menthyl *O*-menthyl dithiocarbonate by treatment with methyl iodide in ether. A solution of the dithiocarbonate (2.46 g) in ether (20 ml) was shaken with 0.5 g of hydrazine hydrate for 3 h and kept for 12 h at 0°C. The ether layer was washed with water and dried, and gaseous HCl was passed through the solution. The hydrochloride formed was soluble in ether. After evaporation of the ether an oil remained which crystallized on cooling and was purified by washing with pentane. Yield 1.0 g. M.p. 126–128°C. (Found: C 49.42; H 8.48; N 10.79. Calc. for $C_{11}H_{23}ClN_2OS$: C 49.53; H 8.63; N 10.51).

VII has also been obtained from *S*-carboxymethyl *O*-menthyl dithiocarbonate (cf. Ref. 8) but yields of the latter (only obtained as an oil) were very low and variable.

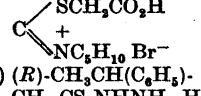
1-Methyl-2-phenylethyl isothiocyanate (VIII) was prepared from commercial, optically active amphetamin sulfate by the thiophosgene method.⁹ The isothiocyanate was obtained as an oil with b.p. 84.5°C at 0.4 mmHg (it

Table 1.

| Nickel complex of: ^a | Circular dichroism | | Absorption spectrum | |
|--|--------------------|--|---------------------|------------|
| | λ_{\max} | $\Delta\epsilon_{\max} \times 10^{-3}$ | λ_{\max} | ϵ |
| (<i>S</i>)-C ₆ H ₅ CH ₂ CH(CH ₃)-NH-CS-N(CH ₃)-NH ₂ (ionic, type I) | 475 555 | 24 22 | 428 | 119 |
| 3(<i>R</i>)-Menthyl-O-CS-NH-NH ₂ (inner complex, type II) | 435 | -6 | 440 | 103 |

^a Solvent: abs. ethanol. No circular dichroism was observed with (*R*)-CH₂CH(C₆H₅)CH₂-CS-NHNH₂ (type I).

Table 2.

| Compound | g in 100 ml | [ϕ] λ^{25} | | | | |
|---|---------------------|---------------------------|-------|--------|--------|--------|
| | | λ (nm) | | | | |
| | | 365 | 436 | 546 | 578 | 589 |
| (III) (<i>R</i>)-CH ₂ CH(C ₆ H ₅)CH ₂ CO ₂ H | 2.2830 ^a | -175° | -106° | -58.7° | -51.1° | -48.8° |
| (IV) (<i>R</i>)-CH ₂ CH(C ₆ H ₅)- CH ₂ -CS-NC ₆ H ₁₀ | 0.8790 ^a | | -778° | -320° | -264° | -247° |
| (V) (<i>R</i>)-CH ₂ CH(C ₆ H ₅)CH ₂ - SCH ₂ CO ₂ H | 1.1520 ^a | -704° | -384° | -211° | -182° | -171° |
|  | | | | | | |
| (VI) (<i>R</i>)-CH ₂ CH(C ₆ H ₅)- CH ₂ -CS-NHNH ₂ ·HCl | 1.0570 ^a | | -297° | -144° | -123° | -114° |
| (VII) 3(<i>R</i>)-Menthyl-O-CS- NHNH ₂ ·HCl | 1.0218 ^b | -471° | -382° | -244° | -216° | -220° |
| (VIII) (<i>S</i>)-C ₆ H ₅ CH ₂ CH(CH ₃)NCS | 1.6975 ^a | | 436° | 242° | 210° | 215° |
| (IX) (<i>S</i>)-C ₆ H ₅ CH ₂ CH(CH ₃)- NH-CS-N(CH ₃)NH ₂ | 0.8363 | -780° | -516° | -307° | -263° | -268° |

^a in abs. ethanol; ^b in diethyl ether.

decomposed on attempts to distill it at 10 mm Hg). (Found: C 67.97; H 6.52; N 8.08; Calc. for C₁₀H₁₁NS: C 67.80; H 6.23; N 7.91).

2-Methyl-4-(1'-methyl-2'-phenylethyl)thiosemicarbazide (IX). A solution of VIII (0.5 g) and methylhydrazine (0.15 g) in ether (*cf.* Ref. 10) yielded 0.20 g of the thiosemicarbazide with m.p. 98–100°C. (Found: C 59.10; H 7.90; N 18.67. Calc. for C₁₁H₁₇N₃S: C 59.19; H 7.62; N 18.83).

The nickel complexes were prepared by adding ethanolic solutions of nickel(II) chloride to ethanolic solutions of the thio compounds.^{1,11} The ionic complexes (type I) were transformed into the inner complex compounds (type II) by addition of NaOH. The inner complexes derived from VI and IX were too insoluble in ethanol for a measurement of the dichroism, so the measurement was only performed with the ionic complex.

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Dehydration of 2,2'-Alkylidene-bis-dimedones to Tetrahydroxanthenes by Reaction with Formic Acid

OVE H. MATTSSON* and
GÖRAN SUNDSTRÖM

Department of Organic Chemistry,
University of Stockholm, Box 6801,
S-113 86 Stockholm, Sweden

Dimedone (5,5-dimethyl-1,3-cyclohexanedione) has for a long time been used as a reagent to characterise aldehydes.^{1,2} The initially formed 2,2'-alkylidene-bis-dimedones can be dehydrated to the corresponding tetrahydroxanthenes *I*.

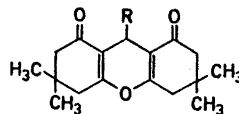
The recommended procedure for the preparation of the anhydro derivatives involves treatment of 2,2'-alkylidene-bis-

dimedones in refluxing ethanol-water (4:1) for 5 min in the presence of hydrochloric acid. This method, however, is not always applicable. Thus, the formaldehyde derivative, methylene-bis-dimedone, does not react under the conditions mentioned above.³ Dehydration of this compound to *Ia* has only been accomplished under vigorous conditions, e.g. by heating at 200°C⁴ or treatment with concentrated sulfuric acid or acetic anhydride at elevated temperatures.^{1,2,5}

We attempted to repeat some of the reported experiments but failed to obtain anything but traces of *Ia*. Dehydration with polyphosphoric acid considerably improved the yield.⁶

In connection with studies on the ring opening of dispiro[5.0.5.1]trideca-1,5,8,12-tetraone it was found that treatment with formic acid yielded anhydro derivatives of certain substituted methylene-bis-1,3-cyclohexanediones.⁶ The general applicability of formic acid as a mild and efficient dehydrating agent to obtain tetrahydroxanthenes of type *I* has now been studied. A number of 2,2'-alkylidene-bis-dimedones were dehydrated at 90–100°C within less than 5 min or at room temperature in 90 min to give pure xanthene derivatives in almost quantitative yields. Methylene-bis-dimedone gives *Ia* in 97% yield on prolonged treatment. Traces of *p*-toluenesulfonic acid or a strongly acidic ion exchange resin increase the rate of formation of *Ia*. The less stable tetrahydroxanthene derived from methylene-bis-1,3-cyclohexanedione was also prepared by this method.

All tetrahydroxanthenes obtained (Fig. 1) give characteristic UV and IR spectra. UV maxima were found in the regions 228–233 nm (log ϵ 4.23–4.34) and 292–302 nm (log ϵ 3.61–3.95). The IR spectra show well-defined bands around 1670, 1630, 1375, 1195, 1165, and 1140 cm⁻¹.



- | | |
|---|---|
| <i>Ia</i> R = H | <i>Ie</i> R = 3-NO ₂ - ϕ |
| <i>Ib</i> R = CH ₃ | <i>If</i> R = 3-OCH ₃ -4-OH- ϕ |
| <i>Ic</i> R = C ₂ H ₅ | <i>Ig</i> R = 3,4-CH ₂ O ₂ - ϕ |
| <i>Id</i> R = C ₃ H ₇ | |

Fig. 1.

* Present address: Kemikoncernen Fosfatbolaget, Liljeholmens Stearinfabriks AB, S-100 61 Stockholm 11, Sweden.