THE REDUCTION OF BENZOINS TO DEOXYBENZOINS WITH Cr(II)

M. PÍŠOVÁ and M. SOUČEK

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague 6

Received April 12th, 1973

The reduction of 4- and 3,4-symmetrically substituted benzoins to corresponding deoxybenzoins with chromous sulfate in a homogenous system dimethylformamide–water, or with Cr(II) bound as a complex onto the polymeric resin Chelex 100 is described. The yields of the reduction are in both cases quantitative.

Deoxybenzoins substituted in positions 4 or 3, 4 by methoxyl or benzyloxyl groups are key intermediates in the synthesis of some degradation products of lignin. These compounds, if both aromatic nuclei are substituted by identical groups, may be obtained with advantage from corresponding benzoins by substitution of the hydroxyl group with hydrogen.

The reduction of benzoin to deoxybenzoin usually requires drastic reaction conditions, as for example prolonged boiling with zinc in acetic acid[1] or with tin in aqueous-alcoholic hydrogen chloride solution[2,3]. The yields of reduction are average but they may be increased by using powdered tin[4]. None of the procedures mentioned gives satisfactory results in cases when the benzoin molecule is substituted with a group sensitive to high concentration of hydrogen ions.

Irreproducible and low yields (27–43%) of reduction of 3,3'-dimethoxy-4,4'-dibenzyloxybenzoins led us to the investigation of reagents the oxidation potential of which would not be higher than the oxidation potential of tin (-0.13 V) and which would be capable of hydrogenolysis of the hydroxy group in benzoins in the pH 4–9 interval. We found that chromous sulfate is such a reagent.

The first attempts at reduction of benzoins were carried out in aqueous ethanol with chromous sulfate generated *in situ* from chromic sulfate and zinc (procedure *A*). The reaction took place slowly and the yields were decreased by adsorption of the product on the zinc powder surface. Therefore we modified the procedure by adding excess chromium(II) sulfate solution to a benzoin solution in dimethylformamide (procedure *B*). The reaction took place immediately and the yields were practically quantitative with all deoxybenzoins. In several cases we used chromium(II) for the reduction, bound as a complex (chelate) to the iminodiacetic acid groups of the Chelex 100 resin (procedure *C*). The yields were again quantitative but the reaction took place slowly. The yields obtained by all three procedures are given in Table I.

TABLE I

Deoxybenzoins $ArCH_2COAr$ Prepared on Reduction of Benzoins $ArCH(OH)COAr$ with Chromous Sulfate by Procedures *A*-*C*

Ar	Yield, % *A*	Yield, % *B*	Yield, % *C*	M.p.[a], °C
C_6H_5	68	95	93	61 – 62
$4\text{-}ClC_6H_4$	76	97	—	130 – 132
$4\text{-}CH_3OC_6H_4$	93	93	95	110 – 111
$3\text{-}CH_3O\text{-}4\text{-}C_6H_5CH_2OC_6H_3$	78	98	94	147 – 148[b]
2-Furyl	81	97	—	20 – 23

[a] The melting points were in agreement with those from the literature[7]. [b] For $C_{30}H_{28}O_5$ (468·5) calculated: 76·92% C, 5·98% H; found: 77·10% C, 5·92% H. ν (CO) 1 668 cm^{-1}.

We used procedure *B* for the verification of the stoichiometry of the hydrogenolytic reaction. In agreement with the reduction of alkyl halogenides with chromium(II) perchlorate[5] the reduction of benzoins to deoxybenzoins requires 2 equivalents of Cr(II). Even when supposing that the reaction intermediate is benzoylphenylmethyl radical, in no case could we observe the formation of the corresponding dimer (*i.e.* 1,2-dibenzoyl-1,2-diphenylethane). The mechanism of reduction of benzoins with Cr(II) ions is evidently different from the reductive dimerisation of triphenyl- and diphenylcarbinols[6].

EXPERIMENTAL

Reduction of Benzoins

Procedure A. Benzoin (1 mmol) was stirred at room temperature with a mixture of $Cr_2.(SO_4)_3.18\ H_2O$ (800 mg, 2 mmol) and zinc powder (650 mg, 10 mmol) in 50% aqueous ethanol (50 – 100 ml; freed from oxygen by heating to boiling point). The reaction course was followed chromatographically on silica gel thin layers in benzene–ethyl acetate 9 : 1. The reaction product was isolated in the usual manner.

Procedure B. To a solution of benzoin (1 mmol) in dimethylformamide (15 – 25 ml) an aqueous solution of chromous sulfate[5] (2·2 mmol) was added using a syringe rinsed with argon. After 5 minutes the reaction mixture was diluted with water and the separated deoxybenzoin filtered off.

Procedure C. Chelex 100 resin (Calbiochem, 10 ml) was stirred with 0·4M-$CrSO_4$ (10 ml) under argon until the blue colour of the solution disappeared. The aqueous phase was decanted and the resin washed with water freed from oxygen (3 × 50 ml). After addition of benzoin solution (1 mmol) in 80% ethanol (50 – 100 ml) the reaction mixture was stirred for 2 hours. Deoxybenzoin was isolated in the usual manner. The yields and the physical constants of the compounds prepared are given in Table I.

Stoichiometry of the Benzoin Reduction

To a solution of benzoin (212 mg, 1 mmol) in ethanol (50 ml) a solution containing the required molar amount of chromous sulfate was added. The consumption of the reagent was determined iodometrically in an aliquot of the reaction mixture. From the remaining reaction mixture benzoin was isolated by column chromatography on silica gel (1 × 15 cm; 15% H_2O content) with benzene–ethyl acetate 9 : 1. The results are the following:

[Cr(II)]/[benzoin]	0·50	1·00	1·50	2·00	2·50
Consumption of Cr(II), mol	0·48	1·05	1·51	1·95	2·48
Decrease of benzoin, mol	0·21	0·45	0·70	0·94	0·92

REFERENCES

1. Kohler E. P., Nygaard E. M.: J. Am. Chem. Soc. *52*, 4133 (1930).
2. Bollard D. A., Dehn W. M.: J. Am. Chem. Soc. *54*, 3969 (1932).
3. Allen J., Buck J. S.: J. Am. Chem. Soc. *52*, 310 (1930).
4. Carter P. H., Cymerman-Craig J., Lack R. E., Moyle M.: J. Chem. Soc. *1959*, 476.
5. Castro C. E.: J. Am. Chem. Soc. *83*, 3262 (1961).
6. Slaugh L. H., Raley J. H.: Tetrahedron *20*, 1005 (1964).
7. *Beilstein's Handbuch der Organischen Chemie,* 4th Ed., Tomes 7 and 19. Springer, Berlin 1920.

Translated by Ž. Procházka.