BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(4), 1167—1168 (1976)

An Improved Synthesis of Dibenzoxanthene

Koki Ota and Taketoshi Kito

Department of Chemistry, Kyushu Institute of Technology, Tobata-ku, Kitakyushu-shi 804

(Received October 2, 1975)

Synopsis 14*H*-Dibenzo[*a,j*]xanthene was easily synthesized by heating alkali (K or Na) 2-naphthyloxide under CO and CO_2 pressure.

14*H*-Dibenzo[*a,j*]xanthene (DBX) and its derivatives have been synthesized by several methods. A mixture of DBX, dibenz[*a,j*]acridine, *N*-formyl-2-naphthylamine, 1-methyl-2-naphthol, and bis(2-hydroxy-1-naphthyl)methane (HNM) was formed by heating a mixture of 2-naphthol and formamide.[1] In this reaction, however, DBX was always not the main product, in addition, it was hard to separate from the other products. 3,11-Dimethyl-14*H*-dibenzo[*a,j*]-xanthene was obtained in a good yield from the reaction of 2-naphthol and formaldehyde, followed by internal cyclization using phosphoryl chloride.[2,3] Now, we wish to report a one-step synthesis of DBX in a higher state of purity.

Results and Discussion

DBX was obtained by heating alkali (K or Na) 2-naphthyloxide in a nonpolar solvent under an atmosphere of CO and CO_2. Such solvents as *N,N*-dimethylformamide and dioxane, in which alkali 2-naphthyloxide dissolves, prevent the reaction. The yield of DBX increases slightly in a reaction of more than 2 h, but the temperature affects the yield considerably. The presence of both CO and CO_2 is essential for the present reaction, and the pressure of CO appreciably affects the yield of DBX. The CO_2 may act as a neutralization agent of alkali salt, in which case the alkali metal would be consumed as alkali carbonate. Thus, the yield of 35% was attained in the reaction at 250 °C for 2 h under a pressure of CO (50 kg/cm^2) and CO_2 (8 kg/cm^2).

Pure DBX was formed as needles when the reaction was carried out in the presence of an alcohol, such as 1-butanol, 1-pentanol, 1-octanol, and 6-methyl-1-heptanol, although the yield of DBX fell slightly upon the alkylation of 2-naphthol by alcohol.[4] For example, the maximum yield of 26.0% was obtained from a reaction at 240 °C for 8 h under pressure of CO (56 kg/cm^2) and CO_2 (10 kg/cm^2) in the presence of octanol; the molar ratio of $C_8H_{17}OH/2\text{-}C_{10}H_7OK$ was 3.5.

Sodium 2-naphthyloxide gave DBX in a poorer yield than the potassium salt.

The thermal stability of DBX was also examined. A mixture of DBX, 1-butanol-*d*, potassium carbonate, and cyclohexane was heated under CO and CO_2 pressure at 240 °C for 1 h; 93.6% of the DBX was recovered and in it no deuterium was found. As a result, it was concluded that DBX is a thermally stable product; in other words, the two methylene hydrogens were thermally inactive under these conditions. On the other hand, at least four deuteriums were found in DBX when a mixture of potassium 2-naphthyloxide, 1-butanol-*d*, and cyclohexane was heated under CO and CO_2 pressure at 240 °C for 2.5 h (this was examined by means of a high-resolution mass spectrometer). Moreover, it was confirmed by NMR analyses that the two methylene protons of this DBX were almost entirely replaced by deuteriums. This fact suggests that the aromatic nucleus is also activated in the transition state and that the two hydrogen atoms in the methylene group of DBX come from both the aromatic nucleus and alcohol.

Experimental

The NMR spectra were obtained on a Japan Electron Optics Laboratory spectrometer (JNM, C-60 HL), with TMS used as the internal standard. The mass spectra were obtained on a Hitachi mass spectrometer (RMU-6L), using an electron-accelerating voltage of 70 eV. The IR spectrum was measured with a Japan Spectroscopic spectrometer (IRA-2).

DBX. One example will be described in detail. In a 300 ml autoclave, with an electromagnetic stirrer, we placed potassium 2-naphthyloxide (4.01 g), and cyclohexane (40 ml). After the air had been replaced by N_2, CO (50 kg/cm^2) and CO_2 (7 kg/cm^2) were introduced into the autoclave. The autoclave was then heated at 250 °C for 2 h. After cooling, aq. 2% NaOH was added to the reaction mixture, and the insoluble product (crude DBX) was filtered on a glass filter. The crude DBX was washed with small amounts of MeOH and then excess water, and the DBX was dissolved with trichloroethylene. The DBX was then obtained as a residue by the evaporation of the trichloroethylene. Yield, 1.09 g (35%, based on potassium 2-naphthyloxide). The melting point, MS, NMR, and IR of this product were consistent with those of authentic DBX.

Analyses of DBX. (i) Elementary analysis, Found: C, 88.91%; H, 4.96%. Calcd for $C_{21}H_{14}O$: C, 89.33%; H, 5.00%. (ii) MS: $M^+=282$ ($C_{21}H_{14}O$), 65%. (iii) NMR (δ value in CS_2 at 24 °C): 4.50, s(2H): 7.1—8.1, m(12H). (iv) IR(cm^{-1}): no absorptions in the range of 1800—1600; 1585, m; 1390, m; 1230, s; 950, m∼w; 800, m; 760, m∼w; 740, m. (v) Mp. 194 °C (from CS_2) determined by DTA.

Thermal Stability of DBX. A mixture of DBX (1.00 g), 1-butanol-*d* (0.58 g), potassium carbonate (0.57 g), and cyclohexane (35 ml) was heated under pressure of CO (34 kg/cm^2) and CO_2 (8 kg/cm^2) at 240 °C for 1 h (the pressure at 240 °C was 82 kg/cm^2). The recovery of the DBX was 93.6%.

*Reaction in the Presence of 1-Butanol-*d. A mixture of potassium 2-naphthyloxide (2.05 g), 1-butanol-*d* (5.20 g), and cyclohexane (40 ml) was heated under pressure of CO (65 kg/cm^2) and CO_2 (10 kg/cm^2) at 240 °C for 2.5 hr. The yield of DBX was 0.35 g. The results of the high resolution mass spectra of the DBX were as follows; *m/e*=282 (62%), 283 (71%), 284 (77%), 285 (45%), and 286 (19%). In the NMR spectrum of this DBX, the ratio of aromatic protons/methylene protons was 0.042. The calculated ratio is 0.167.

Authentic DBX. HNM was prepared according to the directions;[2] DBX was thus obtained, with reference to the synthesis of 3,11-dimethyl-14*H*-dibenzo[*a*,*j*]xanthene,[3] by treating phosphoryl chloride on HNM.

References

1) N. Saito, C. Tanaka, and M. Okubo, *Pharm. Soc. Jpn.*, **76**, 359 (1956).
2) R. Robinson and F. Weygand, *J. Chem. Soc.*, **1941**, 386.
3) R. Royer, *Ann. Chim.*, XII, **1**, 395 (1946).
4) T. Kito and K. Ota, *Chem. Lett.*, **1975**, 1019.