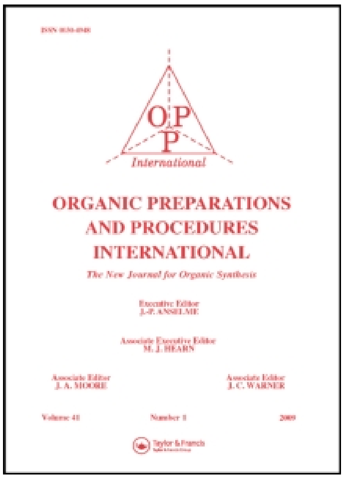

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DIBENZO-[*a*,*j*]-XANTHYLIUM CHLORIDE

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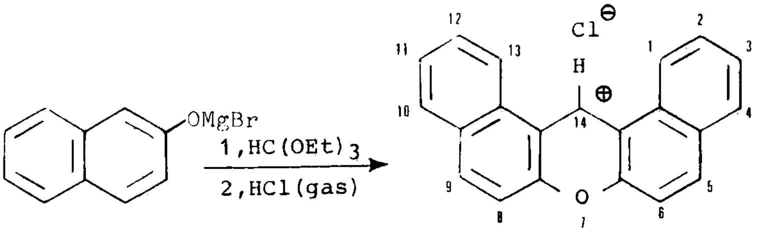
We wish to report a new convenient and efficient procedure for the preparation of a stable carbenium ion chloride directly from 2-naphthyloxymagnesium bromide, ethyl orthoformate and dry hydrogen chloride.[1] This procedure provides the title product in high yield and afford a general synthesis for other dibenzo-[*a*,*j*]-xanthylium derivatives unsubstituted at the 14-position, in addition to those previously described.[2]



To increase the stability and solubility in organic solvents, the chloride is crystallized from acetic acid in the form of an acetic acid monosolvate.

EXPERIMENTAL

Dibenzo-[*a*,*j*]-xanthylium ion. This procedure is typical for the synthesis of dibenzo-[*a*,*j*]-xanthylium derivatives. In a

500 ml, four-necked, round-bottomed flask fitted with a dropping funnel with pressure equalizing side arm, mechanical stirrer, reflux condenser carrying a drying tube, and nitrogen inlet tube, a solution of 0.1 mole of C_2H_5MgBr was prepared from magnesium turnings (2.4 g) and C_2H_5Br (11 g) in 50 ml of anhydrous ethyl ether. A solution of β-naphtol (14.4 g, 0.1 mole) in ethyl ether (150 ml) was added drpwise with vigorous stirring to avoid the formation of clots of 2-naphthyloxymagnesium bromide. The addition required about 15-20 minutes. Stirring was continued for 10 additional minutes, after which ethyl orthoformate (7.0 g, 0.045 mole) in ethyl ether (50 ml) was slowly added and the reaction mixture was gently refluxed for 12-14 hours under a slow stream of nitrogen. After cooling the mixture was quenched with an excess of saturated aqueous ammonium chloride and the aqueous layer extracted twice with 50-ml portions of ethyl ether. The combined organic layer was saturated with a stream of dry hydrogen chloride.

The precipitated orange-red product was collected by suction filtration, washed with a 50 ml portion of ether and dried. The yield of crude dibenzo-[*a,j*]-xanthylium chloride (mixed with some hydrochloride) was 12.5 g, m.p. 203-205°(dec) Recrystallization from 30% HCl gave orange needles of the chloride hydrochloride, m.p. 227-228°(dec), lit.[3] 228-229°. Yield 72% based on ethyl orthoformate. The unreacted β-naphthol (about 2.5 g) was recovered after evaporation of the ethereal mother liquor.

Recrystallization of the crude chloride from glacial acetic acid gave red prisms of the xanthylium salt, acetic acid monosolvate. This salt is very stable and could be stored for some months in a desiccator. The physical characteristics of this salt[4] are: mp. 180°; IR (KBr): main peaks at 1700 (C=O) and 1380 cm^{-1} (xanthyl ether absorption); UV (AcOH): λ_{max} at 307 (log ε = 4.0) and 495 nm (3.92); nmr (CF_3COOD)(100 MHz):(δ) 11.3 broad (s, 1H, H-14), 9.30 (d, 2H, H-1 and H-13), 8.9 (d, 2H, H-5 and H-9), 8.0-8.3 (m, 8H, other aromatic protons), 2.1 (s, 3H, CH_3).[5]

Anal. Calcd. for $C_{23}H_{17}ClO_3$: C, 73.31; H, 4.55; Cl, 9.41.
Found: C, 73.60; H, 4.67; Cl, 9.32.

Starting from 6-bromo-2-naphthol the 3,11-dibromoderivative was prepared; in this run 72 hours of refluxing was required after the addition of ethyl orthoformate. Mp. 210°(dec); yield 72% (as chloride hydrochloride). IR (KBr): main peak at 1380 (xanthyl ether absorption), other at 1580, 1490, 1340, 890, 830 and 800 cm^{-1}; UV (conc H_2SO_4): λ_{max} at 317 (log ε = 4.78), 480 (sh, 4.47) and 500 nm (4.57); nmr (CF_3COOD)(100 MHz):(δ) 11.0 (s, 1H, H-14), 9.07 (d, 2H, H-1 and H-13), 8.83 (d, 2H, H-5 and H-9), 8.2-8.5 (m, 6H, other aromatic protons).[5]

Anal. Calcd. for $C_{21}H_{12}Br_2Cl_2O$: C,49.35; H,2.37; Cl,13.87; Br, 31.27. Found: C, 49.31; H, 2.67; Cl, 13.55; Br, 31.51.

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* To whom inquiries should be directed.

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4. The crystal structure was recently determined: G. D. Andreetti, G. Bocelli, and P. Sgarabotto, *Crystal Structure Communications* 2, 91 (1973).
5. With respect to the spectrum of corresponding 14-H-dibenzo-[*a,j*]-Xanthene, there is a large downfield shift of all the signals (1-2 ppm) due to the distribution of the charge. A detailed analysis of nmr spectra will be published elsewhere.

6) Melting points are uncorrected and were determined on a Büchi capillary melting point apparatus. Infrared spectra were obtained on a Perkin-Elmer 137 Infracord spectrometer. Nuclear magnetic resonance spectra were determined on a Varian XL-100 spectrometer, from TMS as internal standard. Elemental analysis were performed by the Analytical Dept. of the Faculty of Pharmaceutical Sciences of Parma.

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