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A NOVEL SYNTHESIS OF QUINONE-IMONIUM CATION

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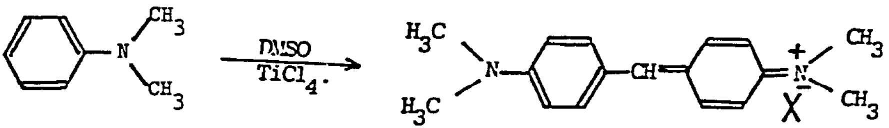
Abstract:

A new method which utilizes Dimethylsulfoxide (DMSO) as methylating agent was invoked for the synthesis of the title compounds. The procedure used proved to be simple and gives a high yield, and also demonstrates a new type of reaction for DMSO.

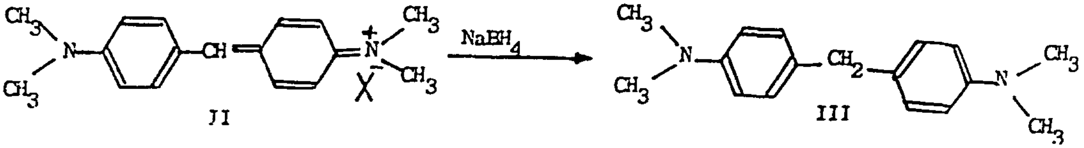
The colored quinone-imonium cations have been prepared by different procedures, and all depend on the oxidation of bis(4,4-dimethylaminophenyl) methane$^{(1-4)}$. In our Laboraotry we found an efficient simple procedure to prepare the colored quinone-imonium cations. This procedure is achieved by simultaneous mixing of N,N-Dimethylaniline and DMSO with Lewis acid ($TiCl_4$ or $FeCl_3$) as a catalyst. The mixture is then heated to ca.150°C and at which the mixture turns blue. After cooling , little amount of water was added, and the blue product was extracted with chloroform. Addition of ether to the chloroform solution results with a precipitate which was then treated with petroleum ether (50-70°C) to give the crystalline product II, with 70% yield.



II (X^-, CH_3SOCH_2)

Compound II was thoroughly characterized as follows. The IR Spectrum (KBr disks) shows the characteristic bands at 1580 cm^{-1} (C=C), 1350 cm^{-1} (C-N) and 2860 cm^{-1} (-CH). The UV-visible spectrum (methanol solution) shows three bands at 590 nm, 310 nm and 264 nm. High resolution mass spectrum shows the following peaks, m/e 253.1712 (M^+; calcd for $C_{17}H_{21}N_2$ 253.3663); 210.1273 (M^+-C_2H_5N; calcd for ($C_{15}H_{16}N$ 210.2981); 134.0976 (M^+-C_8H_9N; calcd for $C_9H_{12}N$ 134.2005); 118.0659 (M^+ -$C_8H_{13}N$; calcd for C_8H_8N 118.1579). The fragmentation pattern is in agreement with the proposed structure. The NMR spectrum in $CDCl_3$ shows signals at; 2.91 ppm(N-CH_3), 3.81 ppm (-CH) and 6.83 ppm and 7.00 ppm for the aromatic moiety.

Qualitative tests give positive result for sulfur and negative for halogens. In addition, the nmr spectrum shows two signals at 2.77 ppm and 3.23 ppm assigned for CH_3-S and $-CH_2^-$ respectively. Reduction of methanolic solution of compound II with sodium-borohydride produced compound III. Pure sample of III was obtained by recrystallization from methanol.



Compound III was thoroughly characterized and identified as follows. The melting point of the compound was 86-88°C without correction (Lit. M.P. 88°C)$^{(2)}$. The IR spectrum (KBr disks) shows the following characteristic bands 1600 cm^{-1}(C=C), 1340 cm^{-1} (C-N) and 1505 cm^{-1} (δ CH_2). Mass spectrum shows the molecular ion peak m/e 254. The NMR spectrum shows the following signals 2.84 ppm (N-CH_3), 3.78 ppm (-CH_2),6.61 ppm and 7.00 ppm for the aromatic protons. The results obtained are in excellent agreement with that reported for compound III.$^{(5)}$

Since other aromatic amines gave similar reactions with DMSO, this together with the above results give a clear indication, that DMSO acts as a good coupling agent for aromatic amines. However, further investigations on this problem are in progress.

Aknowledgment:

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References:

1. V. Sterba, Z. Sagner, M. Matrka, Czech. Chem. Commun. 30(7) 2477 (1965).
2. T.T.Vasileva, R.K. Freidlina, IZV. Akad. Nauk, S.S.S.R.Ser Khim. 5 1093(1968).
3. K.A.Kovar, K.Weihgold. H. Awterhoff, Arch. Pharm. (Weinheim) 304(8) 595 (1971).
4. K. Hellmut, B.Hans. (BASF A-G). Ger. Offen. 2,243 , 322 (1974).
5. The Sadtler handbook or proton NMR spectra P. 275.

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