www.sphinxsai.com
ChemTech
International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.1, No.3 , pp 452-456, July-Sept 2009

Solvent-free Cerium(IV) Ammonium Nitrate Catalyzed Synthesis of 4,4′-Diaminotriarylmethane Leuco Malachite Materials

Ghasem Rezanejade Bardajee*

Department of Chemistry, Payame Noor University, Qazvin Branch,

P.O. Box 878, Qazvin, Iran

Corresponding author e-mail: rezanejad@pnu.ac.ir

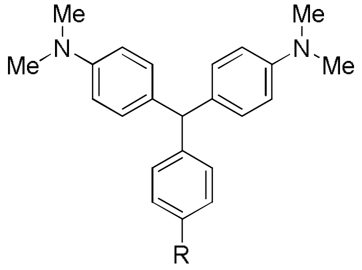
Abstract: We report a simple and efficient procedure for the solvent-free one-step synthesis of 4,4′-dimethylaminotriarylmethanes in the presence of cerium(IV) ammonium nitrate as a Lewis acid catalyst. The entitled compounds were prepared by the tandem regio-selective electrophilic aromatic substitution reaction of N,N-dimethylaniline with aryl aldehydes to form corresponding diaminotriarylmethane compounds in good to excellent yields.

Keywords: Cerium(IV) ammonium nitrate, Dimethylaminotriarylmethane, Solvent-free condition, Synthesis.

1. Introduction

Since the initial report on the synthesis of first dye Mauveine by Perkin in 1856, the dye industry still remains a vibrant and challenging area requiring a continuous flow of new researches because of the quickly changing world in which we live.[1-3]

Dyes may be classified according to chemical structure or by their usage or application method. According to the chemical structure classification, triarylmethane dyes are among the most important dyes. Triarylmethane dyes are monomethine synthetic dyes with three terminal aryl groups, of which at least one, but preferably two or three, are substituted by a donor group para to the methane carbon atom. The most important donor is the dimethylamino group which makes dimethylaminotriphenylmethane (DTM) derivatives. The triarylmethane dyes include a broad range of dyes such as Cresol Red, Bromocresol Green, Light Green SF Yellowish, Victoria Blue BO, Ethyl Green, Brilliant Green, Diaminotriphenylmethane, Fast Green FCF, Green S, Fuchsine acid, Chlorophenol Red, Crystal Violet Lactone, Fuchsine, Pararosaniline, Water Blue, Thymolphthalein, Bromocresol Purple and Aurin. Two significant dyes belonging to DTM class include the well-known Malachite Green and Crystal Violet which are presented in Scheme 1.[1-3] The aforementioned DTMs often show photochromism. For instance, they ionize to a triphenylmethyl cation (or quinoid cation) on UV-light irradiation and thus turning green or blue. This type of photochromism, bringing about remarkable environmental changes from electrically neutral to ionic (cationic) states, can be used for photocontrol of physical properties.[4]



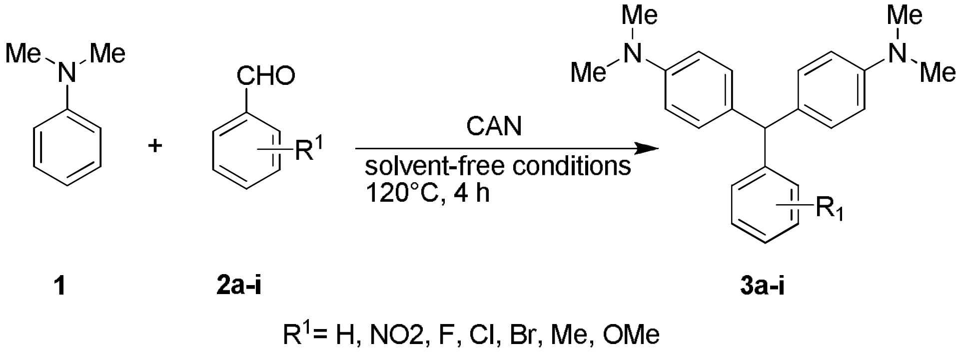
a) R= H: Leucomalachite Green
b) R= $N(Me)_2$: Leucocrystal Violet

Scheme 1.
Two examples of diaminotriphenylmethane (DTM) compounds.

Due to the importance of DTM compounds, several reviews have emerged on di- and triphenylmethane derivatives.[2-5] These compounds have a broad range of applications in color-forming, manufacturing of novel types of various colorless copying papers, pressure-sensitive heat-sensitive materials, high-speed photo duplicating copying papers, light-sensitive papers, ultrasonic recording papers, electrothermic heat-sensitive recording papers, inks, crayons, typewritten ribbons, and photoimaging systems.[2-6] In addition, they have rather specialized applications in biological and analytical purposes.[7-9] For example, they can be employed for detection of hydrogen peroxide in medical diagnostic kits (e.g., glucose determination, by glucose oxidase), in biotechnology process control, in analysis of biological fluids, and in wastewater treatment plants. They not only have antifungal activity and phototoxicity toward tumor cells, but also have been used as copper corrosion inhibitors. Furthermore, they have particular structural properties in solid and solution phases.[10-17]

Survey literature shows that different methods for the preparation of the entitled compounds have been reported including reaction of arene nucleophiles and triethyl orthoformate, or benzhydrol in the presence of acid catalysts, condensation of amines and anilines in acid medium or using zeolites and also by oxidative coupling of anilines with metal catalyst or clay-mediated microwave-assisted from N,N-disubstituted anilines, in which DTMs are obtained in low to modest yields.[18-22] One of the most useful methods for the synthesis of DTMs is the reaction of aryl aldehydes with N,N-dimethylaniline in the presence of an acid such as sulfuric acid, HCl, and *p*-TSA.[21,23-24]

In general, the reported procedures are associated with certain limitations, such as low yields, the use of corrosive acids and excess of solvents, harsh reaction conditions, longer reaction times, and costly reagents, as well as an inconvenience in handling reagents. Considering the above reports, the development of new and simple synthetic methods for the efficient preparation of DTMs is therefore a challenge. In this contribution, we report a simple and efficient method for the preparation of DTM derivatives under solvent-free conditions via applying the cerium(IV) ammonium nitrate (CAN) as a Lewis acid catalyst (Scheme 2).



Scheme 2. CAN catalyzed synthesis of 4,4'-dimethylaminotriarylmethanes

2. Experimental Section

2.1. Materials

Aryl aldehydes, N,N-dimethylaniline and CAN were purchased from Merck or Sigma-Aldrich companies. The solvents were analytical grade and used as received. Silica gel (Merck, grade 9385, 230-400 mesh, 60 Å) for column chromatography was used as received. The course of the synthesis and purity of the products were followed by TLC on silica gel plates (Merck, silica gel 60 F254, ready to use), using ethyl acetate: n-hexane (1:4) as eluent. The eluent for PTLC was the same as TLC eluent.

2.2. Instrumentation

Melting points were determined using a Gallenkamp melting point apparatus and Koffler hotplate and are uncorrected. NMR spectra were recorded on a Brucker 500 MHz FT-NMR spectrometer. ^1H NMR and ^{13}C NMR spectra are referenced to tetramethylsilane and $CDCl_3$, respectively. Chemical shifts are given in ppm. IR spectra were taken as thin films for liquid compounds and as KBr pellets for solids on an ABB Bomem MB-100 FTIR spectrophotometer. IR is reported as characteristic bands (cm^{-1}) at their maximum intensity. Elemental analyses were carried out with Heareus CHN-RAPID instrument.

2.3. General procedure for the synthesis of 4,4'-dimethylaminotriarylmethane derivatives (compounds 3a-k)

A vial equipped with a stir bar was charged with aryl aldehyde (0.5 mmol, 1eq), N,N-dimethylaniline (1.5 mmol, 3eq) and CAN (20 mol %) and the vial was capped. The resulting mixture was heated in an oil bath at 120°C for 4 h, and the course of the reaction was monitored using TLC on silica gel with ethyl acetate: n-hexane (1:4) as eluent. Finally, the reaction mixture was cooled and the crude mixture was purified by column chromatography or PTLC to give the desired product.

2.4. Data for product 3j

Mp. 184-185°C. IR (KBr, cm^{-1}): 3415, 2875, 1612, 1516, 1479, 1447, 1346; ^1H NMR (500 MHz, $CDCl_3$): δ 2.94 (s, 12H, $2N(CH_3)_2$), 3.84 (s, 2H, CH_2), 5.49 (s, 1H, CH), 6.72 (d, J = 8.4 Hz, 4H, 4CH), 7.06 (d, J = 8.4 Hz, 4H, 4CH), 7.19 (d, J = 7.8 Hz, 1H, CH), 7.27 (m, 1H, CH), 7.36 (m, 2H, 2CH), 7.52 (d, $J = 7.5$ Hz, 1H, CH), 7.69 (d, $J = 7.8$ Hz, 1H, CH), 7.76 (d, $J = 7.5$ Hz, 1H, CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 37.4, 41.3, 55.6, 113.1, 119.9, 120.1, 125.4, 126.4, 126.7, 127.1, 128.6, 130.5, 133.6, 140, 142.2, 143.7, 143.8, 144.8, 149.3; Anal. Calcd for $C_{30}H_{30}N_2$: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.19; H, 7.15; N, 6.75.

2.5. Data for product 3k

Mp. 68-69°C. IR (KBr, cm^{-1}): 3412, 2835, 1612, 1521, 1449, 1346; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.85 (s, 6H, $N(CH_3)_2$), 2.96 (s, 6H, $N(CH_3)_2$), 5.13 (s, 1H, CH), 6.61 (m, 4H, 4CH), 6.98 (m, 2H, 2CH), 7.18 (m, 3H, 3CH), 7.28 (m, 4H, 4CH), 7.35 (m, 2H, 2CH), 7.55 (d, $J = 7.6$ Hz, 1H, CH), 7.75 (d, $J = 7.6$ Hz, 1H, CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.9, 52.2, 112.4, 123.9, 125.7, 126.9, 127.2, 127.5, 128.3, 128.5, 128.8, 129.1, 129.5, 130.2, 130.7, 135.3, 139.6, 141.8; Anal. Calcd for $C_{31}H_{30}N_2$: C, 86.47; H, 7.02; N, 6.51. Found: C, 86.59; H, 7.09; N, 6.58.

3. Results and Discussion

Our initial attempts to find the optimal conditions of this reaction employed benzaldehyde and N,N-dimethylaniline under various reaction conditions (Table 1). In the absence of the catalyst, the desired triarylmethane derivative was obtained in trace amount after 20 h (Table 1, entry 1) while good results were obtained in the presence of CAN after 4 h (Table 1, entry 6). Using more than 20 mol% CAN catalyst has less effect on the yield and time of the reaction (Table 1, entry 7).

Table 1. Optimization of the CAN catalyzed model reaction for the synthesis of *Leuco Malachite Green* under solvent-free conditions at 120 °C

Entry	Catalyst (mol%)	Time (h)	Yield (%)^a
1	—	20	10
2	10	5	57
3	20	2	61
4	20	4	67
5	30	3	75
6	30	4	78
7	40	4	80

^{a}Isolated yields

Under the optimized reaction conditions, benzaldehyde (0.50 mmol, 1 equiv), N,N-dimethylaniline (1.50 mmol, 3 equiv), CAN (20 mol %) under solvent-free conditions at 120 °C in a sealed tube for 4 h afforded *Leuco Malachite Green* **3a** in 78% yield (Table 2, entry 1). To generalize this methodology, we subjected a series of other aromatic aldehydes having electron-donating as well as electron-withdrawing substituents to obtain the corresponding triarylmethane derivatives under the optimized reaction conditions (Table 2). The results showed that a wide variety of substituents was tolerated on the aryl aldehydes.

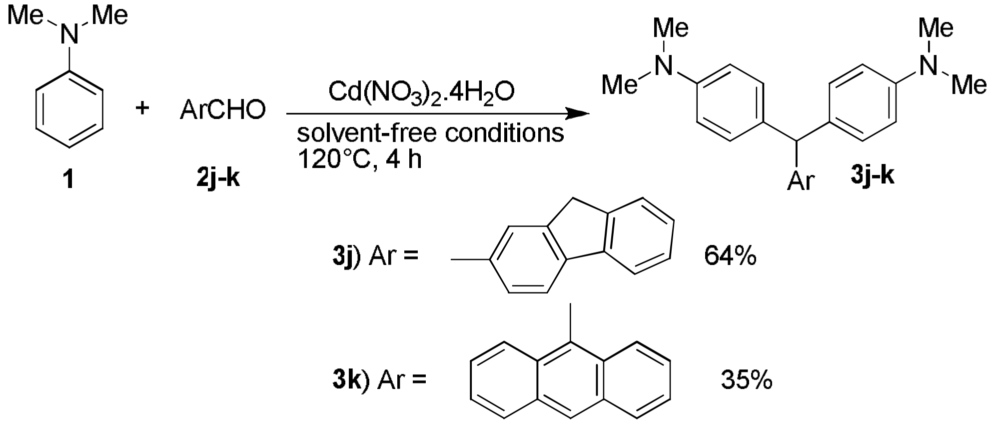
Table 2. CAN catalyzed synthesis of 4,4'-diaminotriarylmethanes **3a-j**[23-26]

Entry	R^1	Product	Mp (°C)	Yield (%)^a
1	H	3a	91-92	78
2	2-NO_2	3b	153-154	90
3	3-NO_2	3c	146-148	85
4	4-NO_2	3d	170-171	95
5	4-F	3e	99-101	86
6	4-Cl	3f	88-89	80
7	4-Br	3g	118-119	78
8	4-Me	3h	108-109	66
9	4-N(Me)$_2$	3i	97-98	55

^{a}Isolated yields

To the best of our knowledge, the dominant mechanism for production of DTMs from the reaction of aldehydes and N,N-dimethylaniline can be summarized in tandem regio-selective electrophilic aromatic substitution reaction. In the aforementioned mechanism, a Lewis acid catalyst like CAN, activates the carbonyl group in aldehyde and increases the rate of reaction via decreasing the activation energy of system. If we accept the aforesaid mechanism, one can expect the general effect of electron donating and electron withdrawing groups on the feasibility of the reaction. In this regard, aromatic aldehydes bearing electron donating groups on the benzene ring should decrease the yield of the reaction while electron withdrawing groups should have an inverse effect. As we expect, aromatic aldehydes with electron withdrawing substituents afforded DTMs in excellent yields (Table 2, entries 2-4). *p*-Halogenated aromatic aldehydes furnished excellent yields of the desired products (Table 2, entries 5-7). On the other hand, with electron-donating substituents good yields of the corresponding DTMs were obtained (Table 2, entries 8-9).

In addition, we explored the scope of the reaction to replace one of the phenyl rings with fused aromatic rings such as 9H-fluorene and anthracene (Scheme 3). Accordingly, 9H-fluorene-2-carbaldehyde and anthracene-9-carbaldehyde were reacted with N,N-dimethylaniline under the usual reaction conditions to afford the desired products **3j** and **3k**, in 64% and 35% yields, respectively. The relatively low yields of the products are rationalized to steric crowding in the resulting DTMs. For more details, the typical ^{1}H NMR and ^{13}C NMR spectra of diaminotriarylmethane leuco base material **3j** along with its assignments are presented in Figure 1. The outlined signals a-e in ^{1}H NMR spectrum, are good evidences for the synthesis of desired compound.



Scheme 3. Synthesis of new DTM derivatives by using fused aromatic aryl aldehydes.

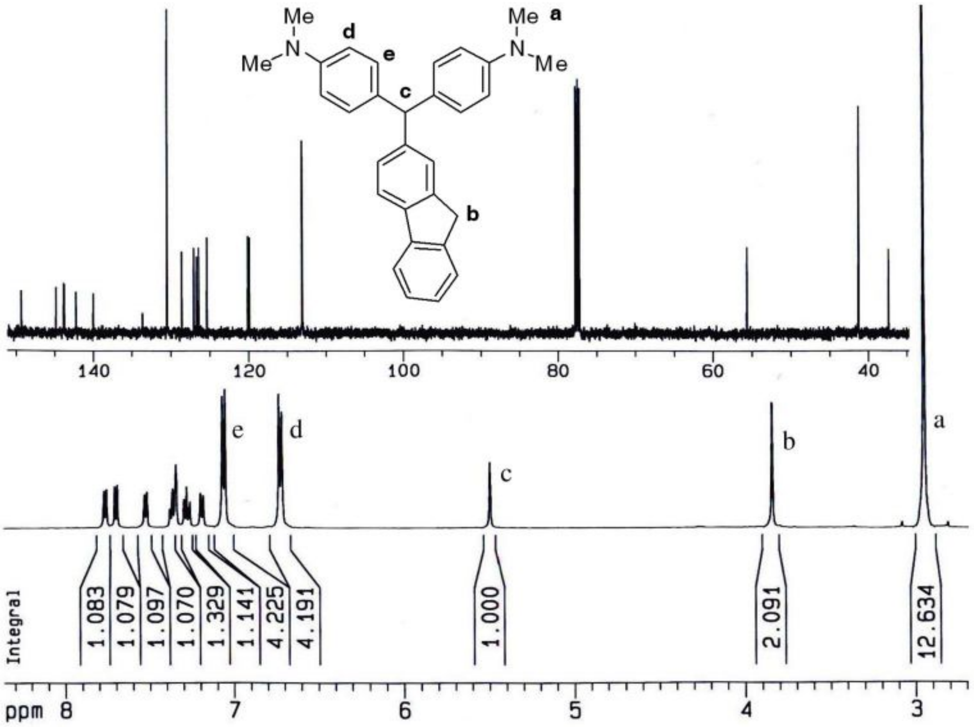


Figure 1. The representative ^{1}H NMR and ^{13}C NMR spectra of 4,4'-diaminotriarylmethane compound 3j

4. Conclusions

We have developed a simple, efficient and versatile methodology for the synthesis of diaminotriarylmethane leuco base materials using catalytic amount of CAN under solvent-free conditions. The simple experimental procedure, solvent-free reaction conditions, and good yields are the advantages of the present method.

Acknowledgements

This research was supported by the Research Council of the Payame Noor University.

References

1. Venkataraman K., The Chemistry of Synthetic Dyes, Academic Press, New York, 1952.Muthyala R., Chemistry and Applications of Leuco Dyes, Kluwer Academic Publishers,New York, 2002.
2. Lubs H.A, The Chemistry of Synthetic Dyes and Pigments, Reinhold Publishing Corporation, New York, 1955.
3. Kimura K., Mizutani R., Yokoyama M., Arakawa R. and Sakurai Y., J. Am. Chem. Soc., 2000, 122, 5448-5454.
4. Duxbury D.F., Chem. Rev., 1993, 93, 381-433.
5. Karukstis K.K. and Gulledge A.V., Anal. Chem., 1998, 70, 4212-4217.
6. Kolpashchikov D.M., J. Am. Chem. Soc., 2005, 127, 12442-12443.
7. Armstrong R.W. and Panzer N.M., J. Am. Chem. Soc., 1972, 94, 7650-7657.
8. Doerge D.R., Chang H.C., Divi R.L. and Churchwell M.I., Chem. Res. Toxicol., 1998, 11, 1098-1104.
9. Dittrich F. and Scholz M., Chem. Abstr., 1986, 107, 112216j.
10. Babb B.E. and Daniel D.S., Chem. Abstr., 1985, 104, 105638h.
11. Culp S.J. and Beland F.A., J. Am. Coll. Toxicol., 1996, 15, 219-238.
12. Cho B.P., Yang T., Blankenship L.R., Moody J.D., Churchwell M., Beland F.A. and Culp S.J., Chem. Res. Toxicol., 2003, 16, 285-294.
13. Maruyama Y., Ishikawa M. and Satozono H., J. Am. Chem. Soc. 1996, 118, 6257-6263.
14. Kawai H. and Nagamura T.J., Photochem. Photobiol. A: Chem., 1995, 92, 105-109.
15. Lueck H.B., McHale J.L. and Edwards W.D., J. Am. Chem. Soc., 1992, 114, 2342-2348.
16. Ichimura K., Funabiki A., Aoki K. and Akiyama H., Langmuir, 2008, 24, 6470-6479.
17. Casiraghi G., Casnati G. and Cornia M., Tetrahedron Lett., 1973, 14, 679-682.
18. Pindur U. and Flo C., J. Heterocycl. Chem., 1989, 26, 1563-1568.
19. Weil H., Sapper E., Kramer K., Kloter H. and Selberg H., Ber., 1928, 61, 1294-1307.
20. Alvaro M., Garcia H., Sanjuan A. and Espla M., Appl. Catal. A: Gen., 1998, 175, 105-112.
22. Lopez-Cortes J.G., Penieres-Carrillo G., Ortega-Alfaro M.C., Gutierrez-Perez R., Toscano R.A. and Alvarez-Toledano C., Can. J. Chem., 2000, 78, 1299-1304.
23. Zhang Z.H., Yang F., Li T.S. and Fu C.G., Synth. Commun., 1997, 27, 3823-3828.
24. Guzman-Lucero D., Guzman J., Likhatchev D. and Martinez-Palou R., Tetrahedron Lett.,2005, 46, 1119-1122.
25. An L.T., Ding F.Q. and Zou J.P., Dyes and Pigments, 2008, 77, 478-480.
26. Pratt E.F. and Green L.Q., J. Am. Chem. Soc., 1953, 75, 275-278.

*****