444 **RESEARCH PAPER** JUNE, 444 JOURNAL OF CHEMICAL RESEARCH 2004

A novel synthesis of tri-and tetra-phenylpyrylium perchlorates from phenyl-substituted cyclopentadienes

Wei-Tao Gong, Xin-Cheng Li, Gui-Ling Ning* and Yuan Lin

Department of Materials Chemistry and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, P.R.China

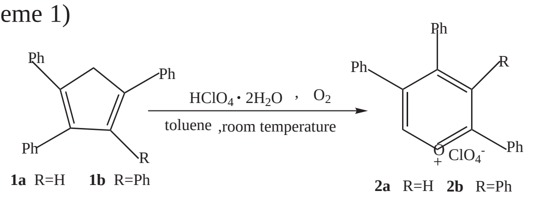
A route to synthesise tri- and tetra-phenylpyrylium perchlorates from phenyl-substituted cyclopentadienes by treatment with perchloric acid and air is described.

Keywords: cyclopentadiene, pyrylium salts, perchloric acid

Pyrylium salts are heterocycles that possess a carbocationic character at the α and γ positions.[1] Because of this property, they have played an important role as versatile synthetic intermediates for complex heterocyclic skeletons,[2] and opened up broad prospects for practical applications, such as Q-switchers, laser dyes, organic luminophores, and secondary nonaqueous-electrolyle battery.[3-6]

Very often, pyrylium cations are obtained by a lengthy stepwise process hinging on the formation and cyclisation of a 1,5-diketone, which typically follows a condensation-dehydrogenation mechanism.[7-8] In contrast, preparation from a ring oxidation is a new approach. In our previous work, we reported the formation of pyrylium salts through the reaction of phenyl-substituted cyclopentadienes with silver(I) perchlorate, where the Ag(I) ion most likely functioned as both an oxidant and a Lewis acid catalyst.[9-10] However, the high price of silver(I) perchlorate and the prerequisite reactive environment restricted its application as a reactant in this approach. Therefore, we tried to use perchloric acid as a substitute. Unfortunately, no pyrylium salts were formed in the absence of air.

On the basis of the above discovery, we report here a novel and efficient method for the synthesis of phenylated pyrylium perchlorates by treatment with perchloric acid and air. (Scheme 1)



When phenyl-substituted cyclopentadiene **1** was stirred in toluene, or a mixed solvent such as dichloromethane/toluene, in the presence of perchloric acid and air, the corresponding phenylated pyrylium cation **2** was obtained in a good yields (>70%) under mild conditions. The product **2** precipitates when toluene only is used as solvent and its work-up procedure was easier. Moreover, a reaction employing pure oxygen proceeded more smoothly and quickly to completion than that using air as the oxidant.

In summary, we have developed a new and facile method for the synthesis of phenyl-substituted pyrylium cations. Because of its operational simplicity, good yield and inexpensive reactant and oxidant, it is worth us investigating its further application in the synthesis of other substituted pylylium compounds.

Experimental

All organic solvents and perchloric acid were used without any further purification; all reactions were carried on at room temperature. Infrared spectra were recorded on a JASCO FT/IR-460plus spectrometer in KBr. ^1H and ^{13}C NMR spectra were determined on an INOVA 400 instrument with acetone-d_6 and DMSO-d_6 as solvents; chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Mass spectra were recorded on a HP 1100 MS spectrometer. Elemental analyses were carried out on a SHIMADZU 6800 instrument.

General procedure: Triphenylsubstituted cyclopentadiene (147mg, 0.5mmol) was dissolved in toluene, enough perchloric acid 72% were added into the solution drop by drop and then the mixture was stirred for a given time (1–2 days) until the reaction proceeded to completion (TLC). The precipitated green powder (crude products) was recovered by suction filtration and washed several times with toluene. It was recrystallised twice using acetic acid and drying for 24h in a vacuum desiccator gave about 112mg of pale yellow crystals. We could also get pure products by reprecipitation from dichloromethane with diethyl ether. Tetraphenylsubstituted cyclopentadiene was reacted by the same process.

CAUTION AND SAFETY NOTE: Organic perchlorates are notoriously unstable and potentially explosive! Only small amounts of materials should be prepared, and these should be handled with great caution.

2a (R=H): pale yellow crystal, yield =71%, m. p. 231–232°C; UV-vis (MeOH) λmax : 342 nm; ^1H NMR (d_6-acetone, 400MHz) δ: 9.17 (s, 1H), 9.09 (s, 1H), 7.45–7.92 (15H); ^{13}C NMR (d_6-DMSO, 100MHz) δ 172.61, 168.85, 163.80, 136.57, 134.84, 133.31, 131.78, 130.98, 130.84, 130.51, 129.52, 129.75, 128.92, 128.62, 127.60, 125.78, 122.63; IR (KBr) δ: 1610.27, 1091.51, 621.93 cm^{-1}; MS (FAB) *m/ z* : 309.1 (M+); Anal . calcd for $(C_{23}H_{17}O^+)(ClO_4^-)$: C 67.57, H 4.19; found C 67.98, H 4.18.

2b (R=Ph): greenish-yellow crystal, yield=72%, m. p. 260–261°C UV-vis (MeOH) λmax : 328 nm; ^1H NMR (d_6-acetone, 400MHz) δ: 9.84 (s, 1H), 7.12–7.67 (20H); ^{13}C NMR (d_6-DMSO, 100MHz) δ: 171.42, 168.13, 163.69, 137.84, 136.69, 133.11, 131.69, 131.15, 130.72, 130.23, 129.76, 129.43, 129.25, 128.90, 128.77, 128.45, 127.77, 127.54, 127.22, 127.04, 125.00; IR (KBr) δ: 1600.12, 1091.51, 621.93 cm^{-1}; MS (FAB) *m/ z* : 385.1 (M+); Anal . calcd for $(C_{29}H_{21}O^+)(ClO_4^-)$: C 71.85, H 4.33, found C 71.96, H 4.31.

We are grateful to the National Nature Science Foundation of China (No. 20072003).

Received 1 March 2004; accepted 20 May 2004
Paper 04/2362

References

1 G.A. Olah. *Angew. Chem. Int. Ed. Engl.*, 1973, **12**, 173.
2 A.T. Balaban, G.W. Ficher, A. Dincylescu, A.V. Koblik, G.N. Dorofeenko, V.V. Mezheritskii and W. Schroth, *Pyrylium salts: synthesis, reactions and physical properties,* eds A.R. Katritzky, *Advances in Heterocyclic Chemistry, Suppl. 2,* Academic Press, New York, 1982.
3 R.F. Khairuutdinov and J.K. Hurst. *Nature.,* 1999, **402,** 509.
4 M. Fakis, G. Tsigaridas, I. Polyzos, V. Giannetas, P. Persephonis. *Chem. Phys. Lett.,* 2001, **342,** 155.
5 P. Nikolov and S. Metzov. *J. Photochem. Photobil. A: Chem.,* 2000, **135,** 13.
6 A.R. Katritzky, P. Czerney and J.R. Levell. *J. Org. Chem.,* 1997, **62,** 8198.
7 V.G. Kharchenko, N.V. Pchelintseve, L.L. Markova and O.V. Fedotova. *Chemistry of Heterocyclic Compounds.,* 2000, **36,** 1007.
8 A.M. Bello and L.P. Kotra. *Tetrahedron Lett.,* 2003, **44,** 9271.
9 X.C. Li, G.L. Ning, L.P. Wu and Y. Lin. *Chinese. Chem. Lett.,* 2002, **13,** 1141.
10 G.L. Ning, X.C. Li, M. Munakata and W.T. Gong. *J. Org. Chem.,* 2004, **69,** 1432.

---

* Correspondence. E-mail: ninggl@dlut.edu.cn