Pergamon

Tetrahedron Letters, Vol. 37, No. 37, pp. 6717-6720, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)01508-0

The Synthesis of Pentadienylium Salts via Reactions of (5-ethoxy-1,5-diaryl-2,4-pentadienylidene)ethyloxonium Perchlorate with Hydrazines

François Rivière, Vadim D. Romanenko, Marie-Rose Mazières, Michel Sanchez, Jean-Gérard Wolf*

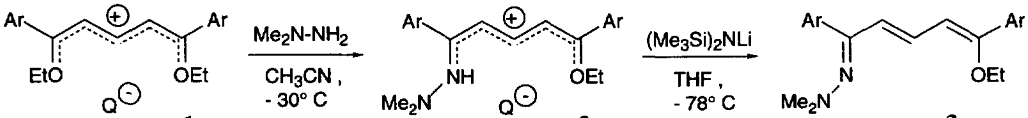
Synthèse et Physicochimie Organique , unité associée au CNRS , Université Paul Sabatier,
118 route de Narbonne, F-31062 Toulouse cedex, France, e-mail: wolf@iris.ups-tlse.fr, FAX (33) 61 55 60 11

Keywords: cyanine dyes; hydrazinium salts

Abstract: Reaction of the readily available (5-ethoxy-1,5-diaryl-2,4-pentadienylidene)ethyloxonium perchlorate **1** with hydrazines, R_2NNH_2 or $RNHNH_2$,provides a simple and efficient synthesis of previously unknown (5-ethoxy-1,5-diaryl-2,4-pentadienylidene)hydrazinium salts **2a-d**. Application of this method to the synthesis of the highly conjugated pentadienylium salt from terephthalic dihydrazide is reported. Copyright © 1996 Elsevier Science Ltd

There is a great interest in the synthesis and properties of charged polyenic linear systems with extended backbone conjugation through $p\pi$-$p\pi$ overlap leading towards potential applications as advanced materials. Species of the type $[R_2N\text{-}(\text{-}CH{=}CH\text{-})_n\text{-}CH{=}NR_2]^+ X^-$ are attracting increasing attention due to their unique physico-chemical properties.[1] We[2] and others[3] have recently shown that the latter are readily prepared by the reactions of open-chain carboxonium salts (derivatives of the 1,5-diaryl-2-pentene-1,5-dione) with primary and secondary amines. In extension of our work directed towards the studies of new types of pentadienylium salts, we now describe the successful implementation of this approach for the preparation of the first representatives of (5-ethoxy-1,5-diaryl-2,4-pentadienylidene)hydrazinium perchlorates that can serve as versatile intermediates in the synthesis of highly conjugated unsymmetrically functionalized charged polyenic compounds.

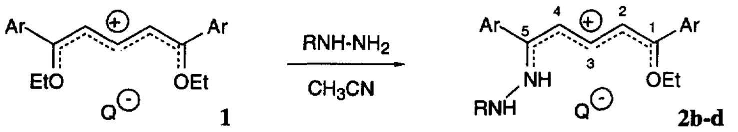
Interaction of the carboxonium salt **1**[4] with N,N-dimethylhydrazine (**a**) in acetonitrile at -30 °C afforded a nearly quantitative yield of the N-(5-ethoxy-1,5-diaryl-2,4-pentadienylidene)-N',N'-dimethylhydrazinium perchlorate (**2a**).[5] No symmetrically disubstituted pentadienylium salt or side products were detected by NMR during the course of this reaction. When **2a** was allowed to react with one equivalent of lithium bis(trimethylsilyl)amide in THF at -78 °C, the corresponding neutral hydrazone **3** was obtained:[5]



1 **2a** **3**

Ar = $pCH_3C_6H_4$- Q = ClO_4

A similar reaction carried out with benzoyl- (**b**), arenesulfonyl- (**c**) or diphenylthio-phosphorylhydrazide (**d**) produced the expected pentadienylium salts **2b-d** in high yields.[6]



b R = PhCO-
c R = pMePhSO$_2$-
d R = Ph$_2$P(S)-

Satisfactory analytical and spectral (^{1}H, ^{13}C NMR, MS) data were obtained for all compounds.[6]

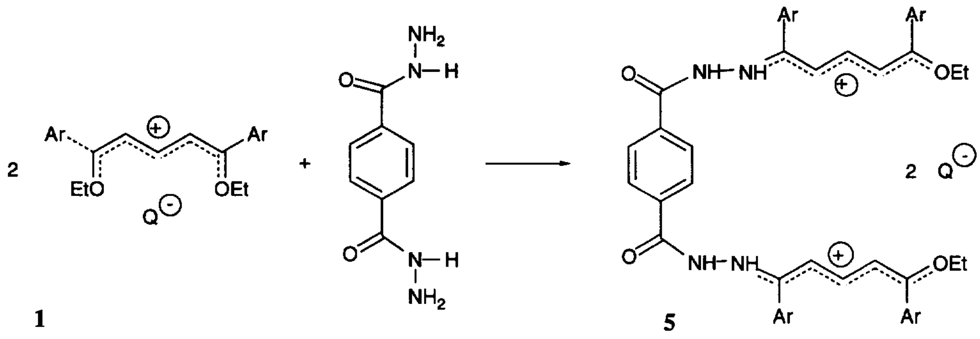
A comparative study of ^{1}H, ^{13}C NMR spectra of the products **2a-d** and the neutral hydrazone **3** shows that in all compounds the three methine proton on the chain (H$_2$, H$_3$ and H$_4$) are coupled in an ABX spin system. The H$_3$ proton is the most deshielded ($7.0 < \delta < 7.5$ ppm) and the vicinal coupling constants ($11 < {}^3J_{HH} < 15$ Hz) are consistent with a *trans-trans* configuration of the polyenic chain. Moreover, the δ ^{13}C shows a positive partial charge on the odd carbon atoms 1, 3 and 5. Specific structural features for these N,N-dimethylhydrazinium derivatives **2a-d** are related with the following potential prototropic equilibrium:

In **II'** forms, the positive charge is located on N$_\beta$ and thus the methine chain appears like a neutral polyenic system. The position of this equilibrium is related to the nature of R and R' as it is demonstrated by UV vis spectroscopy (table **1**). Except for **2c** all spectra in acetonitrile present two $\pi \rightarrow \pi^*$ transition bands corresponding to the forms **II** ($406 < \lambda < 428$ nm) and **II'** ($313.5 < \lambda < 348$ nm) respectively. In the case of electrodonor substituents (R = R' = Me, **2a**) the greater basicity on N$_\beta$ displaces the equilibrium towards **II'a.** The similarity of the UV parameters of **2a** ($\lambda = 315.5$, $\varepsilon = 22\,200$) and the homologous neutral hydrazone **3** ($\lambda = 315$, $\varepsilon = 22\,900$) confirms this assumption. On the other hand, the electroattractive substituents in **2b-c** favours the conjugated form **II**.

Table 1: UV-vis spectra in acetonitrile at 25 °C

Compound	λ nm	ε mol^{-1}.l.cm^{-1}
2a	406.5 313.5	19 500 22 200
2b	427 349	21 000 26 750
2c	435.5 327	23 800 15 900
2d	429 319	32 600 11 750
3	315	22 900

The reaction of **1** with hydrazines provides a potential way to prepare polyfunctional linear pentamethinium salts as it was demonstrated on the example of terephthalic dihydrazide. Treatment of the latter with **1** in a molar ratio 1/2 affords a near quantitative yield of bis-pentamethinium salts **5**.



In conclusion, it should be noted that the reaction described herein gives readily access to a wide range of new pentadienylium salts and serves to further expand the use of (5-ethoxy-1,5-diaryl-2,4-pentadienylidene) ethyloxonium perchlorate as reactive intermediate in organic synthesis.

Acknowledgements: We thank The Paul Sabatier University for its financial support to V.D.R. in the Kiev-Toulouse Exchange Program .

References and Notes

1. Tyutyulkov, N.; Fabian, J.; Mehlhorn, A.; Dietz, F.; Tadjer, A.: "Polymethine dyes, Structure and Properties" *St.Kliment Ohridski University Press, Sofia (Bulgaria)*, **1991.** Marks, T.J.; Ratner, M.A.; *Angew.Chem.Int.Ed.Engl.* **1995**, *34*, 155-173. Reichardt, C.; Harms, K.; Kinzel, M.; Schäfer, G.; Stein, J.; Vacadlo, S.; *Liebigs Ann.* **1995**, 317-327.
2. Payrastre, C.; Obaya, N.; Madaule, Y.; Wolf, J.-G. *Tetrahedron Lett.* **1994**, *35*,3059-3062.
3. Pikus, A.L., Feigel'man, V.M.; Mezheritzkii,V.V. *Zh. Org. Khim.* **1989**, *25*, 2603-2608.
4. Mazières, M.R.; Romanenko, V.D.; Gudima, A.O.; Payrastre, C.; Sanchez, M.; Wolf, J.-G.; *Tetrahedron* **1995**, *51*, 1405-1414.
5. Synthesis of **2a**: To a solution of the carboxonium salt **1** (2 mmol) in dry CH_3CN (20 ml) at -30 °C, Me_2NNH_2 (2 mmol) was added dropwise. The reaction mixture was allowed to stir for 1h followed by evaporation of solvent in vacuum and crystallization of a solid from CH_3CN, orange crystals. Yield: 86%, m.p.114 °C. Elemental analysis: C% calc.: 61.60, found: 60.96; H% calc.: 6.47, found: 6.40; N% calc.: 6.25, found: 6.43. ^1H NMR (CD_3CN) δ ppm: 1.43 (3H, d, CH_3); 2.3 and 2.4 (3H, s, CH_3-Ar); 2.8 (6H, s, $(CH_3)_2N$); 4.2 (2H, q, O-CH_2); 6.3 (1H, d, $^3J_{HH}$ = 12 Hz, H_2); 7.05 (1H, d, $^3J_{HH}$ = 12 Hz, H_4); 7.1 < δ < 7.6 (9H, ArH and H_3); 9.7 (1H, s large, HN). ^{13}C NMR (CD_3CN) δ ppm: 14.6 (CH_3); 21.5 and 21.6 (CH_3Ar); 67.6 (CH_2O); 105.1 (C2); 113.7 (C4); 162.2 (C3); 174.2 (C1); 176.1 (C5). MS (DCI, NH_3) M^+ = 349 (100%).

   Synthesis of **3**: A solution of $(Me_3Si)_2NLi$ in THF [prepared from hexamethyl-disilazane (1 mmol) in THF (10 ml) and BuLi (0.625 ml, 1.6 M, 1 mmol)] was added dropwise to a solution of **2a** in THF (10 ml) at -78 °C. Chromatography (Al_2O_3 neutral, benzene/hexane, 70:30) afforded pure hydrazone **3**. Yellow powder, yield 92%. Elemental analysis: C% calc.: 79.26, found: 79.35; H% calc.: 8.10, found:

8.33; N% calc.: 8.04, found: 7.87. ^{1}H NMR (CD_3CN) δ ppm: 1.42 (3H, t, CH_3); 2.31 and 2.40 (3H, CH_3Ar); 2.54 (6H, s, $(CH_3)_2N$); 4.22 (2H, q, CH_2O); 6.3 (1H, d, $^3J_{HH}$ = 12 Hz, H_4); 7.13, (1H, d, $^3J_{HH}$ = 15 Hz, H_2); $7.1 < \delta < 7.5$ (9H, ArH and H_3). ^{13}C NMR (CD_3CN) δ ppm: 14.6 (CH_3); 21.0 (CH_3-Ar); 47.6 ($[CH_3]_2N$); 64.7 (CH_2O); 102.8 (C2); 120.0 (C4); 137.7 (C3); 162.6 (C1); 164.0 (C5). MS (EI) $M^{+\cdot}$ = 348 (52%); $[CH_3\text{-}C_6H_4\text{-}NH_2]^+$ = 119 (100%).

6. Typical procedure for the preparation of **2b-d**: A solution of hydrazide (1 mmol) in CH_3CN or THF (15 ml) was added dropwise to a solution of **1**(1 mmol) in dry CH_3CN (15 ml). After 3 h, the solvent was removed and the residue was crystallized from CH_3CN.

2b: Yield: 85%, m.p.132 °C; orange crystals. Elemental analysis: C% calc.: 64.06, found: 63.96; H% calc.: 5.57, found: 5.60; N% calc.: 5.34, found: 5.39. ^{1}H NMR (CD_3CN) δ ppm: 1.40 (3H, t, CH_3); 2.3 and 2.4 (3H, s, CH_3-Ar); 4.2 (2H, q, O-CH_2); 6.4 (1H, d, $^3J_{HH}$ = 12 Hz, H_4); 6.9 (1H, d, $^3J_{HH}$ = 14 Hz, H_2); $7 < \delta < 7.7$ (14H, ArH and H_3). ^{13}C NMR (CD_3CN) δ ppm: 14.2 (CH_3); 21.3 and 21.4 (CH_3Ar); 68.5 (CH_2O); 106.9 (C4); 112.1 (C2); 165.8 (C3); 166.0 (C=O); 176.2 (C5); 179.2 (C1). MS (DCI, NH_3) M^+ = 425 (100%).

2c: Yield 83%, m.p.83 °C; orange crystals. Elemental analysis: hygroscopic, accurate values are found whith 0.5 mole H_2O C% calc.: 58.48, found: 57.56; H% calc.: 5.43, found: 5.94; N% calc.: 4.87, found: 5.58.^{1}H NMR (CD_3CN) δ ppm: 1.40 (3H, t, CH_3); 2.3 (3H, s, CH_3-Ar); 2.4 (6H, s, CH_3-Ar); 4.3 (2H, q, O-CH_2); 6.4 (1H, d, $^3J_{HH}$ = 12.5 Hz, H_4); 6.95 (1H, d, $^3J_{HH}$ = 13.5 Hz, H_2); $7.2 < \delta < 7.6$ (15H, ArH and H_3); 8.75 and 9.9 (1H, s, HN). ^{13}C NMR (CD_3CN) δ ppm: 14.2 (CH_3); 21.3 and 21.4 (CH_3Ar); 68.5 (CH_2O); 106.9 (C4); 112.8 (C2); 167.3 (C3); 178.4 (C5); 180.8 (C1). MS (DCI, NH_3) M^+ = 475 (100%).

2d: Yield 81%, m.p.147 °C; orange crystals. Elemental analysis: C% calc.: 62.21, found: 62.80; H% calc.: 5.38, found: 5.37; N% calc.: 4.40, found: 4.52. ^{1}H NMR (CD_3CN) δ ppm: 1.40 (3H, t, CH_3); 2.3 and 2.4 (3H, s, CH_3-Ar); 4.3 (2H, q, O-CH_2); 6.3 (1H, d, $^3J_{HH}$ = 12.5 Hz, H_4); 6.95 (1H, d, $^3J_{HH}$ = 12 Hz, H_4); 7.0 (1H, d, $^3J_{HH}$ = 14 Hz, H_2); $7.1 < \delta < 8.1$ (19H, ArH and H_3); 9.8 (1H, s, HN). ^{13}C NMR (CD_3CN) δ ppm: 14.2 (CH_3); 21.2 and 21.3 (CH_3Ar); 6.9 (CH_2O); 105.9 (C4); 113.8 (C2); 164.5 (C3); 178.4 (C5); 178.6 (C1). MS (DCI, NH_3) M^+ = 537 (100%).

(*Received in France* 9 *July* 1996; *accepted* 30 *July* 1996)