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On the diastereoselective electrogeneration of (2*SR*,3*SR*)-1,5-diaryl-2-(2,2-dichlorovinyl)-3-(trichloromethyl)pentane-1,5-diones from 2,2,2-trichloroethylideneacetophenones. A combined experimental and density functional computational study

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ABSTRACT

Electrochemical reductions of 2,2,2-trichloroethylideneacetophenones under constant cathodic potential in anhydrous acetonitrile–lithium perchlorate followed by addition of water led to previously unknown (2*SR*,3*SR*)-1,5-diaryl-2-(2,2-dichlorovinyl)-3-(trichloromethyl)pentane-1,5-diones in high to near quantitative yields. The molecular structure of a member of this family of compounds, (2*SR*,3*SR*)-(2,2-dichlorovinyl)-1,5-bis(4-nitrophenyl)-3-(trichloromethyl)pentane-1,5-dione, was determined by X-ray crystallography. The formation mechanism of these products has been studied on the basis of chemical, voltammetric and HF and B3LYP computational methods. It corresponds to electrogeneration of dienolate anions, which attack starting material molecules by a Michael addition reaction type.

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1. Introduction

Electroreductions of gem-polyhalogenated have been studied from various focuses [1]. Chloral is an inexpensive multipurpose starting material for organic synthesis [2]. It is able to react with a wide variety of organic compounds to provide derivatives bearing a trichloromethyl group whose electrochemical reduction offers a high synthetic potential that we have studied for several years. This line of work has led to substantial advances in synthetic methodology [3–8]. Cathodic reductions of 2,2,2-trichloroethylideneacetophenones **3** were carried out in the presence of acetic acid, revealing itself as the first synthesis of 1-aryl-4,4-dichlorobut-3-en-1-ones **5** (2,2-dichlorovinylacetophenones), which were obtained in near quantitative yields [6,7]. A main interest of this reaction deals with the exclusive formation of β,γ-unsaturated ketones with total exclusion of the corresponding isomeric α,β-unsaturated ketones. The operating reaction mechanism was studied in detail concluding that dienol intermediates are involved but dienolate anions are not its precursors [7].

In order to increase the knowledge on the electrochemistry of compounds **3**, we now report results on the cathodic reductions of these compounds in an aprotic medium. In contrast to other halogenated compounds, the behaviour of gem-polyhalides in aprotic media has been scarcely investigated, and the majority of previous work, unlike this research, has been mainly directed to study reductions of polyhalides without any additional molecular functionality. Also, the reactions described in this paper are of significant synthetic usefulness since they provide an efficient fully diastereoselective approach to novel (2*SR*,3*SR*)-1,5-diaryl-2-(2,2-dichlorovinyl)-3-(trichlorome-thyl)pentane-1,5-diones **8**, whose structure we have confirmed by X-ray crystallography. As far as we know, this is the first time that an electrochemical approach to 1,5-diketones is reported. Finally, special attention has been devoted to determine the main cause for the observed diastereoselectivity with the aid of Hartree–Fock (HF) and density functional (DFT) computational methods. These methods along with voltammetric measurements have proven very useful to clarify some features of the electrochemical process.

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2. Experimental

2.1. Electropreparative and analytical instrumentation

General equipment has been described elsewhere [6].

2.2. Starting materials

Compounds **3** were prepared as previously described [6].

2.3. General procedure for electroreduction of compounds 3

Preparative experiments were performed following the experimental procedure previously reported for electrolyses in protic media [6] but in the absence of acetic acid as proton donor. Compounds **3** (5 mmol) were reduced under nitrogen atmosphere at cathodic potentials comprised between −0.30 and −0.45 V vs SCE. These potentials were selected in order to provide operative current intensities of 200 mA. The cell voltage values remained below 5 V and the electricity consumption was 1 F mol^{-1} for all cases. Electrolysis products were isolated by removing the solvent under reduced pressure and addition of the residue to cold water. The solid precipitate was collected by filtration and boiled in methanol-activated charcoal. After filtration and evaporation of methanol in vacuo, crude products **8** were isolated and were crystallised from the appropriate solvent (compounds **8b–f**, **i**) or purified by silica gel column chromatography (compounds **8a** and **g** hexane-ether 3:1; compound **8h** hexane-acetone 9:1). After purification, the products were characterised by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, MS and X-ray crystallography. The spectral data for products **8a** and **g** are reported as representative examples of spectroscopic properties of this class of substances. A complete collection of analytical data for all compounds is provided as supplementary information.

*(2SR,3SR)-2-(2,2-Dichlorovinyl)-1,5-diphenyl-3-(trichloromethyl)pentane-1,5-dione (**8a**)*: yield 88%. Crystallisation from petroleum ether gave white needles mp 89–90 °C. ^{1}H NMR *(* (CDCl$_3$, 300 MHz): 3.49 (dd, 1H, J = 18.0 Hz, J = 3.3 Hz), 3.59 (dd, 1H, J = 18.0 Hz, J = 7.0 Hz), 4.70 (td, 1H, J = 7.0 Hz, J = 3.3 Hz), 5.12 (dd, 1H, J = 10.6 Hz, J = 7.0 Hz), 5.76 (d, 1H, J = 10.6 Hz), 7.65–7.84 (m, 6H), 7.99–8.03 (m, 4H). ^{13}C NMR *(* (CDCl$_3$, 75.4 MHz): 38.98 (CH$_2$), 49.87 (CH), 55.14 (CH), 103.24 (CCl$_3$), 125.57 (CCl$_2$), 126.05 (CH), 128.19 (CH), 128.67 (CH), 128.87 (CH), 129.04 (CH), 133.68 (CH), 133.96 (CH), 135.65 (C), 136.32 (C), 195.76 (CO), 195.99 (CO); FAB$^+$: 463 (M$^+$+1); IR (Nujol): 1680, 1597, 1265, 1182, 1066, 987, 900, 891, 781, 765, 711, 686 cm^{-1}; Anal. calcd for $C_{20}H_{15}Cl_5O_2$ (464.60): C 51.70; H 3.25; Found: C 51.72; H 3.22.

(2*SR*,3*SR*)-2-(2,2-Dichlorovinyl)-1,5-bis(4-nitrophenyl)-3-(trichloromethyl)pentane-1,5-dione (**8g**): yield 78%. Crystallisation from methanol gave yellow needles mp 142–143 °C. ^{1}H NMR *(* (CDCl$_3$, 400 MHz): 3.53–3.62 (m, 2H), 4.65–4.70 (m, 1H), 5.11 (dd, 1H, J = 10.6 Hz, J = 7.0 Hz), 5.70 (d, 1H, J = 10.6 Hz), 8.16 (d, 2H, J = 8.9 Hz), 8.18 (d, 2H, J = 8.9 Hz), 8.38 (d, 2H, J = 8.9 Hz), 8.39 (d, 2H, J = 8.9 Hz). ^{13}C NMR *(* (CDCl$_3$, 100.8 MHz): 39.51 (CH$_2$), 50.35 (CH), 55.31 (CH), 102.52 (CCl$_3$), 124.22 (CH), 124.34 (CH), 124.89 (CCl$_2$), 126.99 (CH), 129.28 (CH), 129.67 (CH), 139.97 (C), 140.41 (C), 150.80 (C), 150.88 (C), 194.48 (CO), 194.57 (CO); FAB$^+$: 553 (M$^+$+1); IR (Nujol): 1697, 1685, 1602, 1523, 1344, 1271, 1207, 1105, 1074, 1027, 995, 847, 794, 758, 731, 704 cm^{-1}; Anal. calcd for $C_{20}H_{13}Cl_5N_2O_6$ (554.59): C 43.31; H 2.36; N 5.05; Found: C 43.31; H 2.31; N 4.95.

2.4. X-ray structure determination of compound (8g)

Crystal data: $C_{20}H_{13}Cl_5N_2O_6$, $M_r = 554.57$, monoclinic, space group $P2_1/c$, $a = 7.2614(3)$, $b = 10.6436(4)$, $c = 29.020911$ Å, $\beta = 93.359(2)^\circ$, $V = 2239.10(15)$ Å^3 at 100 K; $Z = 4$, $D_x = 1.6458$ g cm^{-3}, $F(000) = 1120$, $\mu = 0.690$ mm^{-1}. *Data collection*: A colourless needle 0.35 × 0.12 × 0.10 mm was mounted in inert oil on a glass fibre and transferred to the cold gas stream of the diffractometer (Bruker SMART APEX). Measurements were performed to $2\theta_{max}$ 52° with monochromated Mo Kα radiation. Of 24102 measured reflections, 4563 were unique ($R_{int} = 0.026$) and were used for all calculations. *Structure refinement*: The structures were refined anisotropically against F^2 (programme SHELXL-97) [9]. Hydrogen atoms were included with a riding model. The final $wR2$ value was 0.0756 for all reflections and 298 parameters, with $R1$ 0.0298 for reflections with $I > 2\sigma(I)$; max. $\Delta \underline{r}$ 0.397 e Å^{-3}, S 1.05.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the number CCDC 857261. Copies may be requested free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, England (E-mail: deposit@ccdc.cam.ac.uk).

2.5. Voltammetric measurements

Measurements were performed at 298 K with a potentiostat/galvanostat AUTOLAB-100 (Echo-Chemie, Utrecht) using a one compartment three electrode system with a glassy carbon electrode as the working electrode (Metrohm, 3 mm of diameter). A Ag/AgCl/KCl (saturated) electrode was the reference and a glassy carbon bar was the auxiliary electrode. Most experiments were carried out as follows: 5 mM and 1 mM 2,2,2-trichloroethylideneacetophenone solutions in acetonitrile with 0.4 M anhydrous lithium perchlorate as supporting electrolyte were purged with pure argon prior to use. With these prepared solutions, cyclic voltammograms at several scan rates in the interval 0.05 – 5 V s^{-1} were obtained. The electrode was polished between each set of experiments with alumina (BUEHLER Micropolish II (B) gamma alumina 0.05 μm) on an alumina polish pad (BUEHLER microcloth) and then rinsed with purified water. Experimentally acquired voltammograms were subtracted from the background current. Simulations and fitting of cyclic voltammograms were carried out using the software package Digisim (Bionalytical Systems v.3.03).

2.6. Effective electrode area

The effective area of the electrode was determined by chronoamperometry with a 4.0 mM potassium hexacyanoferrate(III) solution ($D = 7.63 \times 10^{-6}$ cm^2 s^{-1}) in 0.1 M potassium nitrate. The electrode area was calculated from the slope of the linear part of the current vs $1/t^{1/2}$ plot by applying the Cotrell equation after background subtraction. The area obtained for the glassy carbon electrode was 0.076 cm^2.

2.7. Computational methods

All computations have been performed with the Spartan'10 package programme [10]. First, the most stable conformers were determined by using the PM3 molecular semi-empirical method. Next, these conformers were used as input for ab initio molecular orbital and density functional theory calculations of geometry optimisations at the Hartree–Fock and Becke, 3-parameter, Lee–Yang–Parr (B3LYP) [11–13] levels of theory with the 6-31G(d) basis set. An excellent agreement was found between the geometries calculated and those obtained from the X-ray crystallographic structure of compound **8g** (data not shown). Frequency calculations were performed at the same level of theory as the geometry optimisations to characterise the stationary points as local minima (equilibrium structures). The effect of the solvent was taken into account by using the SM8 solvation correction model which can be

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