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Cathodic Reduction of 1,2-Dibenzoylchloroethane. Formation of Cyclic Dimolecular Products

Fructuoso Barba* and José Luis de la Fuente

Department of Organic Chemistry, University of Alcala de Henares, Madrid, Spain

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The electrochemical reduction of 1,2-dibenzoylchloroethane in aprotic medium (DMF–$LiClO_4$) on mercury cathode gives four dimeric products. Two of them correspond to cyclic structures, 1-phenyl-*c*-2,*t*-3,*c*-4-tribenzoyl-*r*-1-cyclopentanol (41–43%) and 1-phenyl-*c*-2,*c*-3,*t*-4-tribenzoyl-*r*-1-cyclopentanol (16–18%), and the other two were identified as the racemic and meso 1,6-diphenyl-3,4-dibenzoyl-1,6-butanediones (24–26 and 8–10%, respectively). The dehydration of these products leads to the formation of furans, bisfurans, or cyclopentenes depending on the experimental conditions.

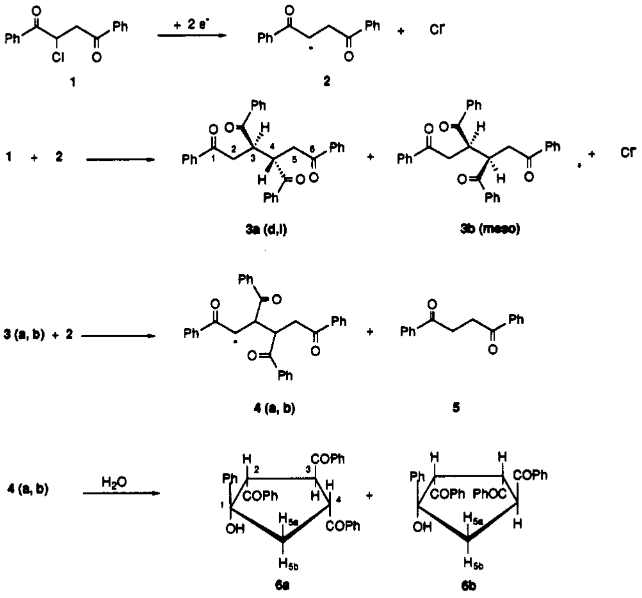
The cathodic reduction of α-halocarbonyl compounds has been intensely investigated during the last few years. Thus, the electrochemical reduction on Hg cathode of phenacyl bromides in aprotic medium gives 2,4-diarylfurans in a very good yields.[1] The formation of these furans can be explained by addition of the electrogenerated anion to the carbonyl group of another molecule of substrate.[2] On the other hand, the cathodic reduction of α-bromopropiophenone surprisingly leads to a dimeric carbonyl compound by a nucleophilic substitution reaction between the electrogenerated anion and the halogenated substrate.[3] Similar results are obtained when the carbonyl group of the phenacyl bromides are protected as the corresponding semicarbazone.[4]

In this paper we describe the cathodic reduction of 1,2-dibenzoylchloroethane (**1**) in aprotic medium. We have found different dimeric products. The synthesis of these compounds from the reduction of 1,2-dibenzoylethylene with a heterogeneous combination of zinc and glacial acetic acid,[5,6] with P(III) esters[7] or catalytic hydrogenation on Pd–C and Pt,[8] was described in the literature. Only one attempt of metal reduction of **1** has been previously reported but dimeric products were not found in the process.[5]

Results and Discussion

The electrochemical reduction of **1** with DMF–$LiClO_4$ as system solvent–electrolyte support on mercury cathode gives different dimolecular products. Separation of the mixture obtained in the reduction is exceedingly difficult and involves laborious fractional crystallizations. Two of these products, **6a** and **6b**, corresponding to 1-phenyl-*c*-2,*t*-3,*c*-4-tribenzoyl-*r*-1-cyclopentanol and 1-phenyl-*c*-2,*c*-3,*t*-4-tribenzoyl-*r*-1-cyclopentanol, give yields of 41–43% and 16–18%, respectively. The other products are identified as racemic 1,6-diphenyl-3,4-dibenzoyl-1,6-butanedione (**3a**) (yield 24–26%) and meso 1,6-diphenyl-3,4-dibenzoyl-1,6-butanedione (**3b**) (yield 8–10%). A minor product, 1,4-diphenyl-1,4-butanedione (**5**) is isolated in 6–7% yield. The yields of the reaction products in all cases could only be determined approximately because of the difficulty of separating the mixture.

Scheme I



The first step of the synthetic route involves transfer of two electrons to the substrate **1** with C–Cl bond cleaveage and formation of enolate anion **2**. This electrogenerated anion attacks the halogen atom of another molecule of substrate adsorbed on the electrode surface to give **3a** and **3b**. These dimeric products have acidic hydrogens. With the formation of these dimeric products, the enolate anion continues to be generated on the electrode. This anion serves as a base for abstraction of a proton from the dimers in solution, giving rise to two new anions **4a**,**b** and compound **5**. These anions finally undergo an intramolecular cyclization to give cyclopentanes **6a** and **6b**. The process can be summarized as outlined in Scheme I.

Structural Study

The conformational behavior of five-membered rings is generally accepted to be more complex and less well understood than that of six-membered rings. The reason

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[•] Abstract published in *Advance ACS Abstracts*, November 15, 1993.

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Table I. NMR Spectral Data of Compounds 6a, 6b, and 7 in $CDCl_3$

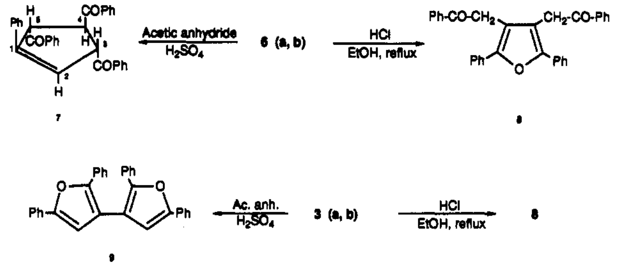
		6a		6b		7	
pos		δ_H (mult, J (Hz))	δ_C	δ_H (mult, J (Hz))	δ_C	δ_H (mult, J (Hz))	δ_C
1	OH	5.29 (s)	84.84	5.24 (s)	84.44		134.32
2		4.89 (d, 9.7)	58.60	4.54 (d, 3.8)	57.73	6.28 (dd, 3.2, 1.3)	128.04
3		5.53 (dd, 9.7, 5.5)	50.14	5.39 (dd, 7.3, 3.8)	51.60	4.78 (ddd, 3.6, 3.2, 1.2)	50.27
4		4.30 (ddd, 11.2, 5.5, 2.4)	49.81	4.67 (ddd, 12.0, 7.5, 3.8)	50.02	5.14 (t, 3.6, 3.6)	54.12
5	a	2.93 (dd, 13.9, 11.2)	47.03	3.07 (t, 13.7, 12.0)	48.49	5.84 (ddd, 3.6, 1.3, 1.2)	59.45
	b	2.51 (dd, 13.9, 2.4)		2.56 (dd, 13.7, 7.5)			
aromatics		8.04–7.10 (m)	142.82–124.68	8.04–7.0 (m)	143.61–124.89	8.01–7.19 (m)	143.83–124.13
	C=O		202.43 201.36 199.71		201.03 200.45 200.41		199.25 198.95 195.12

for this is thought to be associated with the flexible nature of five-membered rings which permits rapid pseudorotation involving interconversion of numerous conformations of similar energies. In view of this, assignment of relative configurations of ring carbon atoms based on vicinal ^1H NMR coupling constants is risky. The relative stereochemistry of the cyclopentane ring carbon atoms was delineated by a series of NOE measurements. NOE experiments were performed on **6a** and **6b** in $CDCl_3$. Furthermore, all the cyclopentane protons, except H5a and H5b, could be confidently assigned by analysis of ^1H NMR spectra. The observed NOE enhancements of **6a** were in agreement with a *trans* relationship between pairs of adjacent protons (H2, H3, and H4). The most significant NOE effects were observed for H3 and the proton of the OH group upon irradiation of H5b which illustrated their relationship, and for H2 and H4 on irradiation of H5a, consistent with these three protons being on the same face of the molecule. These results also allowed for the conclusive assignment the H5a and H5b protons. The NOEs measured for compound **6b** were not as successful as those of **6a** due to isomerization between these two epimers in solution. However enhancements of H4 and OH by irradiation of H5b and of H2 while saturating H3 confirmed the absolute stereostructure of **6b** with H2, H3, and H5a in the *cis* disposition. This structure is in accordance with the chemical shift values of the protons involved. Thus H2 and H3 resonate at higher fields while H4 resonates at a lower field with respect to the protons of **6a** due to the shielding effect exerted by different positions of the benzoyl groups attached to the cyclopentane ring. The ^1H and ^{13}C NMR data of compounds **6a**, **6b**, and **7** are summarized in Table I. The assignment of carbon resonances has been made on the basis of direct ^1H–^{13}C correlation (HETCOSY) and DEPT NMR experiments.

By using ^1H NMR and analytical HPLC, we observed the different isomerizations that **6a** and **6b** undergo in solution ($CHCl_3$, CH_2Cl_2, etc.). Thus compound **6a** rearranges to the open-chain tetraketone **3a**, keeping C3 and C4 in the *trans* configuration. In the same way, compound **6b** isomerizes to **6a**. In this case, the benzoyl groups on carbons 3 and 4 undergo a configurational change presumably through an enolic equilibrium. From the above results, it is evident that these five-membered ring structures have low stability. For this reason the formation of cyclopentanes from **3b** is unlikely, though is possible mechanistically.

Different dehydrations were carried out on the electrochemical products obtained. Thus the dehydration of either cyclopentanes **6a** and **6b** or tetraketone **3a** and **3b** at reflux in HCl/ethanol led to the furan **8** in good yield. On the contrary, when **3a** and **3b** were dehydrated with H_2SO_4 and acetic anhydride, the bisfuran **9** was obtained. Using similar conditions **6a** and **6b** gave **7** as the major product. Theoretically two isomeric cyclopentene products ought to have formed but only **7** was obtained. These reactions are shown in Scheme II.

Scheme II



Experimental Section

General Methods. The ^1H and ^{13}C NMR spectra were determined at 300 and 75 MHz, respectively, using the solvent signal as internal standard. Chemical shifts are expressed in ppm referenced from deuteriochloroform and J values are in hertz. The heteronuclear (HETCOSY) shift correlation experiments were performed by using standard Varian pulse sequences. Mass spectra were obtained by EI at 70 eV. Reagents and solvents were obtained from FLUKA AG and were used without purification. Yields are given for isolated crystalline products.

Electrosynthesis and Isolation. Anode: Pt. Anolyte: $LiClO_4$ (3 mmol) in DMF (15 mL). Cathode: Hg pool. Catholyte: $LiClO_4$ (7 mmol) in DMF (15 mL). The electrolysis cell was a divided cell thermostated at 15 °C and equipped with a magnetic stirrer containing a piece of glass tubing with a glass frit of medium porosity at one end (anode compartment). Solid Na_2CO_3 (2.0 g) was added to the anode compartment for *in situ* neutralization of the perchloric acid generated.

The starting substrate **1** was prepared by the usual procedures.[9] A solution of **1** (5 mmol in 20 mL of DMF) was added to the cathodic compartment and a potential of -0.8 V vs ECS was applied. The consumed charge was 1 F mol^{-1}. The electrolysis was carried out using a potentiostat with an electronic integrator. The reaction time was around 50 min.

The cathodic solution was slowly poured over ice water, precipitating a white solid (1.138 g) which was filtered and washed several times with water. The solid was then slurried in hot ether (2 × 50 mL). The insoluble solid remainig was filtered and contained a mixture of **6a** (major product) and **3b**. These compounds were then partially separated by fractional crystallization from methanol, the first fraction crystallizing quickly from solution being largely **6a** (0.481 g) and the last fractions yielded the tetraketone **3b** (0.106 g). The ethereal solution filtrate was left stand 24 h, and the crystalline solid formed was filtered. In this case a mixture of **6b** and **3a** was obtained and was separated by fractional crystallization from ethanol. The first fraction consisted chiefly of **3a** (0.292 g) and the final ones of **6b** (0.183 g). From the ether filtrate a small amount of diketone **5** (0.071

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[9] Vogel A. I. *Practical Organic Chemistry*, 3rd ed.; Longman: 1956.

g) was isolated. The separation of the reaction products by chromatography on silica gel or alumina using CH_2Cl_2 or $CHCl_3$ as eluent was not satisfactory due to isomerization of the cyclopentanols which has been previously explained.

1-Phenyl-*c*-2,*t*-3,*c*-4-tribenzoyl-*r*-1-cyclopentanol (6a): colorless crystals, crystallized from methanol; mp 158–160 °C; IR (KBr) 3329, 1676, 1641, 1448, 1234 cm^{-1}; MS (EI) *m/z* (rel int) 474 (M$^+$, 0.5), 456 (2), 369 (1.5), 352 (2), 351 (2), 105 (100), 77 (84.5); ^{1}H and ^{13}C NMR Table I. Anal. Calcd for $C_{32}H_{26}O_4$: C, 80.99; H, 5.52. Found: C, 80.82; H, 5.55.

1-Phenyl-*c*-2,*c*-3,*t*-4-tribenzoyl-*r*-1-cyclopentanol (6b): colorless crystals, crystallized from ethanol; mp 201–203 °C; IR (KBr) 3458, 1682, 1652, 1447, 1227 cm^{-1}; MS (EI) *m/z* (rel int) 474 (M$^+$, 0.5), 456 (3), 369 (4), 352 (3.5), 351 (3), 105 (100), 77 (45.5); ^{1}H and ^{13}C NMR Table I. Anal. Calcd for $C_{32}H_{26}O_4$: C, 80.99; H, 5.52. Found: C, 80.89; H, 5.56.

Racemic 1,6-diphenyl-3,4-dibenzoyl-1,6-butanedione (3a): colorless needless, crystallized from ethanol; mp 166–167 °C; IR (KBr) 1681, 1672, 1230 cm^{-1}; MS (EI) *m/z* (rel int) 474 (M$^+$, 0.5), 456 (1.5), 369 (2), 352 (1.5), 351 (1), 238 (1), 105 (100), 77 (77); ^{1}H NMR ($CDCl_3$) δ 3.23 (2H, dd, $J_{2-2'}$ = 18.1 Hz and J_{2-3} = 10.1 Hz, H2 and H5), 3.90 (2H, dd, $J_{2'-3}$ = 2.4 Hz, H2′ and H5′), 4.46 (2H, ddd, H3 and H4), 7.26–8.04 (20 H, m, H arom); ^{13}C NMR ($CDCl_3$) δ 35.93 (CH_2), 40.94 (CH), 128.14–136.25 (C arom), 197.88 and 200.47 (CO). Anal. Calcd for $C_{32}H_{26}O_4$: C, 80.99; H, 5.52. Found: C, 81.10; H, 5.49.

Meso 1,6-diphenyl-3,4-dibenzoyl-1,6-butanedione (3b): colorless crystals, crystallized from methanol; mp 201–202 °C; IR (KBr) 1682, 1672, 1223 cm^{-1}; MS (EI) *m/z* (rel int) 474 (M$^+$, 1), 456 (12.5), 369 (8), 352 (7.5), 351 (8), 105 (100), 77 (40); ^{1}H NMR ($CDCl_3$) δ 3.27 (2H, dd, $J_{2-2'}$ = 18.1 Hz and J_{2-3} = 9.1 Hz, H2 and H5), 3.75 (2H, dd, $J_{2'-3}$ = 3.3 Hz, H2′ and H5′), 4.55 (2H, ddd, H3 and H4), 7.24–7.94 (20H, m, H arom); ^{13}C NMR ($CDCl_3$) δ 39.68 (CH_2), 42.51 (CH), 128.08–137.34 (C arom), 197.63 and 201.33 (CO). Anal. Calcd for $C_{32}H_{26}O_4$: C, 80.99; H, 5.52. Found: C, 81.12; H, 5.54.

1,4-Diphenyl-1,4-butanedione (5). The physical and spectroscopic data are in accordance with those described in the literature.[10]

Dehydration with Acetic Anhydride–Sulfuric Acid. **6a** (0.20 g) was suspended in 15 mL of acetic anhydride and 6 drops of concd sulfuric acid were added. The mixture was then heated for 20 min at 60 °C and was poured over ice water. The aqueous solution was neutralized with sodium hydroxide and extracted with ether (3 × 15mL). The extract was dried (anhydrous Na_2SO_4) and evaporated to dryness under reduced pressure. Cold methanol was added to the crude product and a brown solid precipitated which was chromatographed (silica gel, CH_2Cl_2) to give 0.162 g of **7** in 84% yield.

1-Phenyl-*r*-3,*t*-4,*c*-5-tribenzoyl-1-cyclopentene (7): yellow needless, crystallized from methanol; mp 179–181 °C; IR (KBr) 1676, 1595, 1578, 1446, 1240, 1222, 1214, 702 cm^{-1}; MS (EI) *m/z* (rel int) 456 (M$^+$, 3.5), 352 (14), 351 (51), 230 (3.5), 106 (13.5), 105 (100), 77 (48); ^{1}H and ^{13}C NMR Table I. Anal. Calcd for $C_{32}H_{24}O_3$: C, 84.19; H, 5.30. Found: C, 84.10; H, 5.34.

A solution of 0.200 g of **3a** (or **3b**) in 15 mL of acetic anhydride and 2 drops of concd sulfuric acid was left to stand for 15 min and worked up as in the earlier case to give 0.198 g of solid product. This product contained two components which were separated by column chromatography on silica gel (14 cm × 2 cm, 230–400 mesh) with CH_2Cl_2–hexane (1:1) as eluent. The major component was identifed as **9** (0.152 g, 82%) and the minor one as **8** (0.025 g, 13%).

3,3′-Bis-2,5-diphenylfuran (9): yellow-white crystals, recrystallized from ethanol; mp 194–195 °C; IR (KBr) 1598, 1488, 1476, 1051, 932, 691 cm^{-1}; MS (EI) *m/z* (rel int) 440 (M$^+$ + 2, 7), 439 (M$^+$ + 1, 34), 438 (M$^+$, 100), 333 (6), 105 (30), 77 (30); ^{1}H NMR ($CDCl_3$) δ 6.74 (2H, s, H4 and H4′), 7.79–7.18 (20H, m, H arom); ^{13}C NMR ($CDCl_3$) δ 109.90 (C4 and C4′), 116.35 (C3 and C3′), 123.87–130.84 (C arom), 148.86 (C5 and C5′), 152.78 (C2 and C2′). Anal. Calcd for $C_{32}H_{22}O_2$: C, 87.64; H, 5.05. Found: C, 87.55; H, 5.09.

2,5-Diphenyl-3,4-diphenacylfuran (8): yellow-white crystals, recrystallized from ethanol; mp 163–164 °C; IR (KBr) 1695, 1212, cm^{-1}; MS (EI) *m/z* (rel int) 456 (M$^+$, 5), 351 (3), 105 (100), 77 (55); ^{1}H NMR ($CDCl_3$) δ 4.34 (4H, s, CH_2), 7.98–7.26 (20H, m, H arom); ^{13}C NMR ($CDCl_3$) δ 116.35 (C3 and C4), 126.24–136.15 (C arom), 150.06 (C2 and C5), 196.96 (CO). Anal. Calcd for $C_{32}H_{24}O_3$: C, 84.19; H, 5.30. Found: C, 84.28; H, 5.27.

Dehydration with Hydrochloric Acid in Ethanol. **6a** (or **6b**) (0.20 g) in 20 mL of ethanol and 6 drops of concd hydrochloric acid were refluxed for 5 h. The resulting solution was cooled and a crystalline product appeared. After standing for 1 h and filtering, 0.192 g of product was obtained. This product was separated into two components by chromatography as described above. The products obtained from the dehydration obtained were the furan **9** as major product (0.175 g, 91%) and the bisfuran **8** (0.016 g, 8%) as the minor component. Identical products and similar yields were found when this dehydration reaction was carried out with **3a** (or **3b**).

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[10] *Dictionary of Organic Compounds*, 5th ed.; Chapman and Hall: New York, 1982; Vol. 2, p 2301 and references cited therein.