SHORT PAPER

J. Chem. Research (S), 2002, 118–119

First synthesis of propano-dibenzo [1,3]-dioxocin type compounds from condensation of *p*-substituted phenol derivatives with glutaraldehyde in trifluoroacetic acid

Ali Rahmatpour

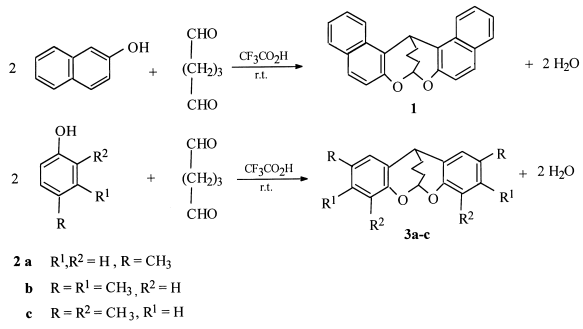
Polymer Chemistry Department, Research Institute of Petroleum Industry, Tehran 18745-4163, Iran

Condensation reactions of glutaraldehyde bisulfate with *p*-substituted phenols and 2-naphthol in trifluoroacetic acid produce propano-dibenzo[1,3]dioxocin type compounds and 8,16-propano-16H-dinaphtho[2,1-d:1′,2′-g][1,3]dioxocin in good yields.

Keywords: glutaraldehyde, trifluoroacetic acid

Some of the dialdehydes and especially their synthetic equivalents are interesting reactive precursors in organic chemistry and are considered as useful starting materials for the preparation of the thermally stable polymers.[1-7] Glutaraldehyde or its salt as a very reactive dialdehyde has been used as a cyclisation reagent for the preparation of heterocyclic ring compounds.[8-10] Condensation of glutaraldehyde bisulfate with 2-naphthol in the presence of formic acid as catalyst at 50–60°C with the formation of 8,16-propano-16H-dinaphtho[2,1-d:1′,2′-g][1,3]dioxocin **1** in only 21% yield has also been reported.[8] In continuation of our research on the synthesis of thermally stable polymers from polymerisable monomers and condensation of diphenols with dialdehydes[7,11,12] we needed to synthesise some model compounds from the condensation of phenols with glutaraldehyde. The possibility of using the reported method for condensation of 2-naphthol and glutaraldehyde bisulfate on different phenols under the same conditions was studied. It was observed that this method cannot be applied to phenolic compounds and the yields of the reactions were found to be very low (< 10%). We therefore decided to develop a new synthetic method for condensation of *p*-substituted phenolic compounds with glutaraldehyde bisulfate. We have reported the possibility of using trifluoroacetic acid as a suitable medium for the condensation of phenols with malonal- dehydetetramethyl acetal and 2,5-dimethoxytetrahydrofuran as very reactive protected dialdehydes.[13, 14] This paper now reports the first synthesis of propano-dibenzo [2,1-d:1′,2′-g] [1,3]dioxocin type compounds from condensation of phenols with glutaraldehyde bisulfate using trifluoroacetic acid as both solvent and catalyst (Scheme 1). The condensations of *p*-substituted phenols **2a–c** with glutaraldehyde bisulfate in trifluoroacetic acid were examined. The reactions were found to be effective and the compounds **3a–c** were obtained in good yields. The overall yields of these reactions are given in Table 1.

The possibility of using our method for the condensation of 2-naphthol and glutaraldehyde bisulfate was also studied. It was observed that the yield of compound **1** was increased to 59%. Condensation of two moles of phenols **2a–c** with glutaraldehyde bisulfate occurs first through a Friedel–Crafts reaction (one carbonyl group) followed by an intramolecular acetalisation reaction as suggested for the condensation of phenols with malonaldehyde-tetramethyl acetal and 2,5-dimethoxytetrahydrofuran.[7,13] The condensation of unsubstituted phenols with glutaraldehyde bisulfate in trifluoroacetic acid produces insoluble resins. Dimeric products **3a–c** and **1** could not be obtained by the reactions of glutaraldehyde solution with compounds **2a–c** and 2-naphthol.



2 a $R^1,R^2 = H, R = CH_3$
b $R = R^1 = CH_3, R^2 = H$
c $R = R^2 = CH_3, R^1 = H$

Scheme 1

Table 1 Condensation of phenolic compounds **2a–c** and 2-naphthol with glutaraldehyde bisulfate in trifluoroacetic acid

Substrate	Reaction time[a]/h	Product (yield[b]/%)	M.p./°C
2-Naphthol	4	**1**(59)	231–232
2a	3.5	**3a**(71)	185–186
2b	4	**3b**(68)	239–240
2c	5	**3c**(64)	194–195

[a] All of the reactions were carried out at room temperature.
[b] Yields refer to isolated products.

The structure of all compounds **3a–c** were deduced from their IR, ^{1}H, ^{13}C NMR and mass spectral data. The IR spectra show no carbonyl and hydroxyl groups. The ^{1}H NMR spectra show a multiplet in the region δ 1.8–2.5 assigned to the methylene, a triplet in the region δ 3.65–3.85 assigned to the hydrogen on the diarylmethyl carbon and also a triplet in the region δ 5.9–6.05 ppm assigned to the hydrogen on the acetal carbon. The ^{13}C NMR spectra show two aliphatic resonances for the diarylmethyl in the region δ 26.8–28 and acetal carbons at region δ 92.4–93.8 ppm respectively, consistent with the overall mirror symmetry.

In conclusion, the simplicity of this method, good yields, readily available starting materials and the possibility of applying this method to phenols and naphthols make this method very useful for this type of transformation in organic synthesis.

* To receive any correspondence.
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

Experimental

Melting points were determined with a Buchi 535 melting point apparatus. UV spectra were recorded on a Pharmacia Biotech Ultraspec 3000 model 80-2160-20 spectrometer, IR spectra on a Perkin-Elmer IR-157-G spectrometer, ^1H, ^{13}C NMR spectra on a 250 MHz Bruker Avance DPX-250 spectrometer using tetramethylsilane (TMS) as an internal standard and mass spectra with a GCMS-QP 1000 EX at 70 eV (Shimadzu). Glutaraldehyde and other chemicals were obtained from the Merck chemical company.

Glutaraldehyde bisulfate: To a solution of sodium bisulfate (30%) was added glutaraldehyde in 2 /1 mole ratio at room temperature. The bisulfate adduct was precipitated by addition of ethanol to the solution and dried in vacuo at 60°C.

General procedure: Phenolic compounds **2a–c** or 2-naphthol (100 mmol), glutaraldehyde bisulfate (50 mmol) and trifluoroacetic acid (10–20 ml) were mixed and allowed to stand for 3.5 to 5h at room temperature. The reaction mixture solidified gradually. After addition of acetic acid (20–30 ml), the crude product was collected by filtration, washed with methanol and boiled with water. The products were further purified by recrystallisation.

8,16-Propano-16H-dinaphtho [2,1-d:1′,2′-g][1,3]dioxocin **1:** White solid, m.p. 231–232°C (from acetic acid)(lit.,[8] 230–232°C), yield 59% (Found: C, 85.15; H, 5.66. $C_{25}H_{20}O_2$ requires C, 85.22; H, 5.68); ν_{max} (KBr) 3000–2905, 1240, 1160, 1070 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 5.4(1H, t, 16-H), 7.4(1H, t, 8-H), 1.5–2.5(6H, m, CH_2), 7-8.2(12H, m, Ar); *m/z* (EI) 352 (5.7), 296(6.7), 281(11.5), 205(11), 168(14), 119(8.5), and 43 (100%).

2,10-Dimethyl-6, 12-propano-12H-dibenzo [2,1-d:1′,2′-g][1,3]dioxocin **3a:** White solid, m.p. 185–186°C (from acetic acid), yield 71% (Found: C, 81.38; H, 7.04, $C_{19}H_{20}O_2$ requires C, 81.42; H, 7.14); UV (CH_2Cl_2) λ 290 (log ε = 4.48), 240 nm (log ε = 4.38); ν_{max} (KBr) 2990–2900, 1240, 1185, 1070 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.85–2.45 (12H, m, -CH_3, -CH_2), 3.82 (1H, t, *J* 1.4 Hz, 12-H), 6 (1H, t, *J* 2.1 Hz, 6-H), 6.45–6.8 (4H, m, Ar); δ_C (62.9 MHz, $CDCl_3$) 22.6 (CH_3), 28 (12-C), 33.1, 33.8, 34.25 (CH_2), 93.8 (6-C), 118.2, 128.4, 129.5,130.5 and 131.6 (Ar), 151.5 (=CO); *m/z* (EI) 280 (45, MH^+), 251 (46), 227 (40), 147 (100), 135 (24), 107 (19), 83 (76), 57 (18), 44 (9.8%).

2,3,9,10-Tetramethyl-6,12-propano-12H-dibenzo[2,1-d:1′, 2′-g][1,3]dioxocin **3b:** White solid, m.p. 239–240°C (from acetic acid), yield 68% (Found: C, 81.7; H, 7.68, $C_{21}H_{24}O_2$ requires C, 81.81; H, 7.79); UV (CH_2Cl_2) λ 293 (log ε = 4.35), 235 (log ε = 4.31); ν_{max} (KBr) 3000-2900, 1234, 1165, 1080 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.8–2.4 (18H, m, -CH_3, -CH_2), 3.7 (1H, t, *J* 1.3Hz, 12-H), 5.95 (1H, t, *J* 1.8 Hz, 6-H), 6.5–6.8 (4H, m, Ar); δ_C (62.9 MHz, $CDCl_3$) 19.2,19.85 (CH_3), 26.8 (12-C), 33.2, 33.6, 34.1 (CH_2), 92.4 (6-C), 117, 124, 128.1, 129.5 and 136.4 (Ar-C), 149.6 (=CO); *m/z* (EI) 308 (14, MH^+), 280 (7.5), 255 (100), 237 (14), 186 (22), 161 (41), 149 (55), 135 (100), 107 (29), 91 (45), 43 (80%).

2,4,8,10-Tetramethyl -6,12-propano-12H-dibenzo [2,1-d: 1′,2′-g][1,3]dioxocin **3c:** White solid, m.p. 194–195°C (from acetic acid), yield 64% (Found: C, 81.6; H, 7.5, $C_{21}H_{24}O_2$ requires C, 81.81; H, 7.79); UV (CH_2Cl_2) λ 291 (log ε = 4.45), 240 (log ε = 4.4); ν_{max} (KBr) 2995–2900, 1230, 1175, 1065 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.75–2.4 (18H, m, -CH_2, -CH_3), 3.68 (1H, t, *J* 1.6Hz, 12-H), 6 (1H, t, *J* 1.8 Hz, 6-H), 6.35–6.7 (4H, m, Ar); *m/z* (EI) 308 (11, MH^+), 255 (100), 237 (15), 186 (12), 161 (32), 149 (12), 135 (21), 91 (24), 43 (100%).

The Department of Chemistry of Shiraz University is thanked for the recording of spectroscopic data.

Received 1 June 2001; accepted 17 September 2001
Paper 01/924

References

1 E.C.M. Coxwoth, *Can. J. Chem*., 1967, **45**, 1777.
2 R.W. Layer, *J. Heterocycl. Chem*., 1975, **12**, 1067.
3 A. Rosenthal and A. Zaionchkovsky, *Can. J. Chem*., 1960, **38**, 2277; A. Chwala and W. Bartek, Monatsh., 1951, 82, 652.
4 O. Dischendorfer, *Monatsh*., 1940, **73**, 45.
5 X. Fan, T. Yamai, H. Okazaki, M. Yamaye, H. Mizobe, Y. Kosugi and T. Kito, *J. Org. Chem*., 1995, **60**, 5407.
6 P. Maravigna, *J. Polym. Sci. Polym. Chem. Ed*., 1988, **26**, 2475.
7 A. Rahmatpour, unpublished work.
8 A. Acuner Tunca, N. Talinli and A. Akar, *Tetrahedron*, 1995, **51**, 2109.
9 O. Mitsunobu and M. Yamada, *Bull. Chem. Soc. Jpn*, 1967, **40**, 2380.
10 A.L. Weis and V. Rosenbach, *Tetrahedron Lett*., 1981, **22**, 1453.
11 A. Banihashemi and B. Pourabbas, *Eur. Polym. J*., 1998, **34**, 1809.
12 A. Banihashemi and B. Pourabbas, *Eur. Polym. J*., 2000, **36**.
13 A. Rahmatpour and A. Banihashemi, *Tetrahedron*, 1999, **55**, 7271.
14 A. Rahmatpour and A. Banihashemi, *J. Chem. Res*., 1999, **6**, 390.