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AIMED SYNTHESIS OF SELECTIVE FLOTATION COLLECTORS CONTAINING THE 1,3-BENZODIOXOLE SYSTEM (°)

Riassunto — *Sintesi mirata di collettori di flottazione selettivi contenenti il sistema 1,3-benzodiossolico.* Viene descritta la sintesi di nuovi collettori contenenti il sistema 1,3-benzodiossolico variamente sostituito nelle posizioni 2 e 5, molto efficaci per la flottazione selettiva di minerali di piombo quali galena e cerussite in presenza di minerali di zinco e d'altri materiali di ganga.

Abstract — The synthesis of new collectors, containing the 1,3-benzodioxole system variously substituted in the positions 2 and 5, aimed at the selective flotation of lead minerals like galena and cerussite in presence of zinc minerals and other gangue materials, is reported.

Key words — Benzodioxoles - Flotation - Collectors.

Flotation is an important industrial technique for the recovery of finely ground valuables, although the possibility of an efficient separation of mixtures of different minerals is strongly dependent on the availability of selective collectors. Such chemical products, whose task is to selectively interact with the particle surface and to cause the transfer of the particle from the aqueous suspension to the froth, are the object of intense researches, chiefly pursued on empirical basis due to the complex nature of the subject.

Our contribution deals with the synthesis of tailor-made collec-

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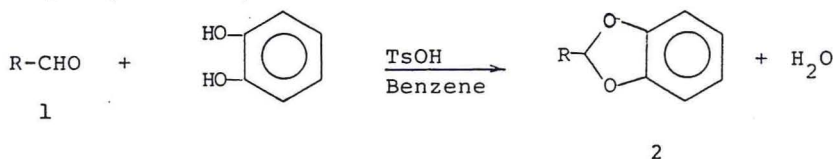
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tors for a given mineral based on a simplified model of the morphology of a substance that, interacting with coordination vacancies at the surface of the water-suspended mineral particles, depresses their superficial solvation and enhances, through proper chemical functions, their affinity for the hydrophobic layers of the froth purposely produced with suitable frothers.

This work concerns the synthesis of new collectors, containing the 1,3-benzodioxole system combined with different functions, aimed at the selective flotation of lead minerals like galena and cerussite in presence of zinc minerals like blende and smithsonite and other gangue minerals. The reported collectors, either containing or not a hydrophobic hydrocarbon tail, show very interesting activities allowing the recovery of lead minerals in high yields and indicating that structures able of axial interactions with the particle play an important role, owing to their enhanced shielding effect towards the solvent. The detailed study of the action of the prepared collectors on mineral suspensions, for specificity and bulkiness of the subject, will be reported in subsequent papers.

1,3-Benzodioxoles substituted in 2-position with an alkyl group were prepared through the condensation of catechol with the proper aldehyde (Scheme 1).



a: R = *n*-butyl; b: R = *n*-hexyl; c: R = *n*-octyl; d: R = *n*-decyl

Scheme 1

The removal of the water was carried out by azeotropic distillation. The molecular structure of the prepared compounds resulted in agreement with elemental analysis, Mass, ¹H-NMR, and IR spectra. All the compounds **2a-d** follow the fragmentation pattern already observed for simpler 2-alkyl-1,3-benzodioxoles showing the base peak at *m/z* = 121 (C₇H₅O₂) that corresponds to the loss of the alkyl group (BROPHY *et al.*, 1980).

The Table 1 collects yields and characteristic data of the prepared 2-substituted benzodioxoles.

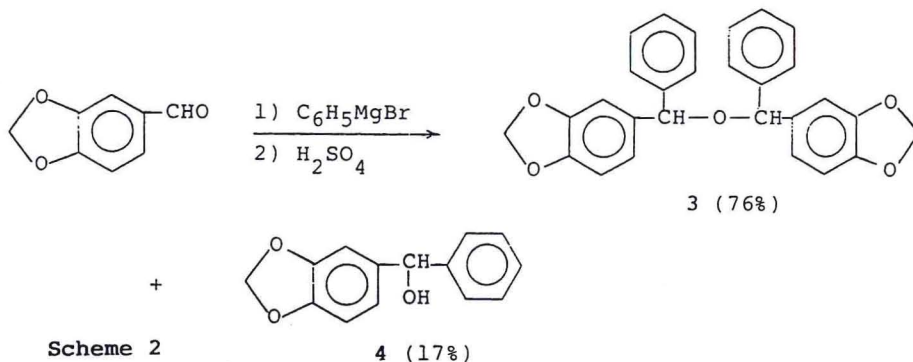
Useful collectors corresponding to 1,3-benzodioxoles substituted in the 5-position are the ether **3** and the diester **9**. The ether **3** was prepared from 3,4-methylenedioxybenzaldehyde and phenylmag-

TABLE 1 - Yields and physical and spectral data of 1,3-benzodioxoles 2a-d.

Compound	Yield %	bp °C/Torr	Mass m/z (%)	¹ H NMR δ (ppm)	IR ν (cm ⁻¹)
2a	48	80/0.025	178 (8,M ⁺), 121 (100)	0.95 (t, 3H),	1484, 1232, 733
				1.45 (m, 4H),	
				1.95 (m, 2H),	
				6.10 (t, 1H),	
				6.77 (s, 4H)	
2b	39	100/0.7*	206 (3,M ⁺), 121 (100)	0.90 (t, 3H),	1484, 1235 735
				1.31 (m, 6H),	
				1.53 (m, 2H),	
				1.95 (m, 2H),	
				6.10 (t, 1H)	
2c	18	100/0.1	234 (7,M ⁺), 121 (100)	6.78 (s, 4H)	1487, 1235, 737
				0.90 (t, 3H),	
				1.31 (m, 12H),	
				1.91 (m, 2H),	
				6.04 (t, 1H),	
2d	47	142/0.35	262 (5,M ⁺), 121 (100)	6.70 (s, 4H)	1482, 1234,735
				0.90 (t, 3H),	
				1.28 (m, 16H),	
				1.90 (m, 2H),	
				6.04 (t, 1H),	
				6.70 (s, 4H)	

 * Lit. (BOESEKEN *et al.*, 1932) 155 °C/20 Torr

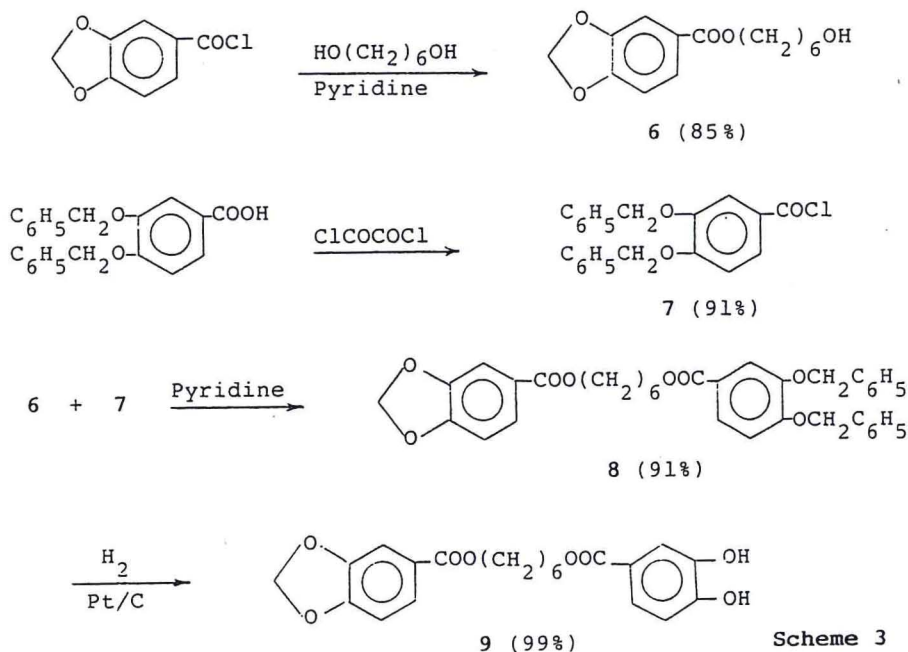
nesium bromide according to scheme 2, by carrying out the hydrolysis under dehydrating conditions.



The molecular structure of **3** was in agreement with elemental analysis, NMR, IR and Mass spectra, with the comment that the electron impact mass spectrum shows fragments at m/z 227 ($\text{C}_{14}\text{H}_{11}\text{O}_3$) and 211 ($\text{C}_{14}\text{H}_{11}\text{O}_2$) corresponding to the ether bond cleavage, and that only the Fast Atom Bombardment (FAB) technique reveals the molecular ion in the protonated form. Moreover, the reaction hydrolysis in scheme 2, performed with a saturated aqueous solution of ammonium chloride, afforded the alcohol **4** with 96% yields. Such alcohol through pyridine chlorochromate oxidation yielded the known (3,4-methylenedioxyphenyl)phenyl ketone (**5**) (SEMMEHACK *et al.*, 1974) and by dehydration with *p*-toluenesulphonic acid in boiling benzene afforded the ether **3**, in analogy with the behaviour of the diphenylmethanol (PRATT *et al.*, 1949).

The synthesis of the diester **9** required the preliminary preparations of 3,4-methylenedioxybenzoyl chloride from 3,4-methylenedioxybenzoic acid (PETER *et al.*, 1982) and of 3,4-bis [benzyloxy] - benzoic acid from 3,4-dihydroxybenzoic acid (SHIMIZU *et al.*, 1951) through protective esterification of the carboxylic function, etherification of the phenolic groups with benzyl chloride and hydrolysis of the ester. The diester **9** was then synthesized from the prepared reagents according to Scheme 3.

The monoester **6** is obtained in good yields simply using an excess (1:6) of 1,6-hexanediol. The protection of the 3,4-dihydroxybenzoic acid with benzyloxy groups resulted essential for our purposes because in its absence the preparation of the 3,4-dihydroxybenzoyl chloride mainly afforded polymeric products, and attempts of direct esterification of the alcoholic group of **6** with the unprotected



3,4-dihydroxybenzoic acid in presence of pyridine and dicyclohexylcarbodiimide failed. The formation of the diester **8** was easily achieved at room temperature in 10 minutes. The deprotection of **8** to **9** by hydrogenolysis resulted very efficient. The molecular structure of **9**, deduced from the synthesis pattern, was in agreement with elemental analysis, $^1\text{H-NMR}$, IR and Mass spectra. It is remarkable that compounds **8** and **9** melt with formation of liquid crystals, the existence intervals of their mesophases, observed under polarized light at the Kofler apparatus, being 65-75 °C and 121-126 °C respectively.

Even if flotation studies will be reported separately, it is interesting to mention that with a milled fraction of crude ore containing lead (6.41%) and zinc (9.20%), characterized by such a granulometry that the 80% of particles ranges between 10 and 100 micron, compound **2c** (200 g/T) in presence of Na_2S (400 g/T) and of Cyanamid Aerofroth 65 (50 g/T) allowed the recovery in one flotation step of 88% of the lead at a concentration of 72% and only of 3% of the zinc. Moreover, in confirmation of the importance of the chemical functions introduced in the 1,3-benzodioxole system compound **9**, tested under analogous flotation conditions as reported

above, showed zero selectivity and 100% efficiency in causing the total flotation of valuables and gangue materials.

EXPERIMENTAL SECTION

Melting points were determined on a Reichert Thermovar Kofler apparatus and are uncorrected. IR spectra were recorded on a 1330 Perkin Elmer spectrophotometer as films or KBr pellets. The reported IR bands, unless otherwise stated, are tentatively assigned on empirical basis to the benzodioxole system. $^1\text{H-NMR}$ spectra were run on a Varian XL 100 or Bruker 300 spectrometers in CDCl_3 (TMS as internal reference) unless otherwise indicated. Mass spectra were determined with a Hewlett Packard 5995 A Gas/Mass spectrometer operating at 70 eV. FAB Mass spectra were determined on a VG ZAB 2HF instrument using a neutral Xenon atom beam of 9.5 KeV. Microanalyses were carried out on a Carlo Erba Elemental Analyzer mod. 1106 of the Department of Chemistry in Arcavacata, the purity of the compounds was estimated to be $\pm 0.3\%$.

1,3-BENZODIOXOLES **2a-d**

A mixture of catechol, aldehyde (molar ratio 1.65:1) and a few crystals of p-toluenesulphonic acid in dry benzene (650 ml/mol of aldehyde) was refluxed in a Dean-Stark apparatus up to ceased evolution of water (about 9 h), then it was treated with excess of petroleum ether (bp 40-60 °C) to precipitate the residual catechol. The filtered solution was eluted through a Merck grade I alumina column (diameter 2.5 cm, height 14 cm) and the solvent evaporated. The pure 1,3-benzodioxoles were obtained by distillation at reduced pressure.

BIS [(3,4-METHYLENEDIOXYPHENYL) PHENYLMETHYL] ETHER (**3**) and (3,4-METHYLENEDIOXYPHENYL) PHENYLMETHANOL (**4**)

A stirred 0.81M solution of phenylmagnesium bromide in diethyl ether (40 ml) was treated dropwise in 90 minutes under nitrogen at room temperature with a solution of 3,4-methylenedioxybenzaldehyde (3.74 g, 24.91 mmol) in dry diethyl ether (90 ml). The mixture was stirred at room temperature for 4 h, dropped into an excess

of 1:1 sulphuric acid efficiently cooled at 0°C and extracted with diethyl ether (5×20 ml). The extracts, after drying over anhydrous sodium sulphate and removal of the solvent, were chromatographed on a Merck silica gel column (diameter 3.2 cm, height 53 cm, 70-230 mesh) to afford in the fractions eluted with benzene the compound **3** [4.14 g, 9.44 mmol; yield 76%; mp 116-118 °C (diethyl ether); IR (v, cm⁻¹ 1489, 1242, 739; ¹H-NMR (δ, ppm): 5.32 (s, 2H, methyne), 5.91 (s, 4H, methylene), 6.77 (d, 2H), 6.82 (m, 4H), 7.33 (m, 10H); mass spectrum, m/z (%): 227 (24), 211 (93); FAB ms, m/z 439 (M⁺+1)] and in the fractions eluted with chloroform the compound **4** [(0.95 g, 4.16 mmol; yield 17%; oil)]. IR (v, cm⁻¹): 3380 (OH); 1481, 1239, 742. ¹H-NMR (δ, ppm): 2.47 (s, 1H, OH), 5.70 (s, 1H, methyne), 5.90 (s, 2H, methylene), 6.75 (d, 1H), 6.82 (m, 2H), 7.35 (m, 5H). Mass spectrum, m/z (%): 228 (27, M⁺). The same reaction repeated under identical conditions but hydrolyzed with saturated aqueous solution of ammonium chloride afforded 5.15 g (22.56 mmol) of the alcohol **4** (91% yield), while the chromatography did not reveal traces of the ether **3**.

DEHYDRATION OF **4**

The alcohol **4** (1.39 g, 6.09 mmol) and a few crystals of p-toluenesulphonic acid in dry benzene (40 ml) were refluxed for 4 h in a Dean-Stark apparatus. The removal of the solvent at reduced pressure afforded an oil that, chromatographed as reported in the previous preparation, gave 0.05 g (0.22 mmol) of the unreacted alcohol **4** and 1.23 g (2.81 mmol) of the ether **3** (yield 96%).

OXIDATION OF **4** TO (3,4-METHYLENEDIOXYPHENYL) PHENYL KETONE (**5**)

A mixture of pyridine chlorochromate (COREY *et al.*, 1975) (2.16 g, 10.02 mmol), grinded Merck 4A molecular sieves (3.5 g) and methylene chloride (5 ml) was treated dropwise under stirring with a solution of the alcohol **4** (1.53 g, 6.70 mmol) in methylene chloride (10 ml). The mixture was stirred at room temperature for 5 minutes, then filtered and the solid residue washed with methylene chloride (10 ml). The combined organic phases were evaporated at reduced pressure, treated with diethyl ether, decolourized with charcoal and

crystallized at -20°C . White crystals of **5** [0.95 g, 4.20 mmol; yield 63%; mp $54-55^{\circ}\text{C}$ (Lit. (SEMMEHACK *et al.*, 1974) $55-56^{\circ}\text{C}$)] were obtained. IR (ν , cm^{-1}): 1640 (CO); 1480, 1235, 737. $^1\text{H-NMR}$ (δ , ppm): 6.11 (s, 2H, methylene), 6.90 (d, 1H), 7.51 (m, 6H); 7.78 (dd, 1H). Mass spectrum, m/z (%): 226 (18, M^+).

1,6-HEXANEDIOL 1-(3,4-METHYLENEDIOXYBENZOATE) (**6**)

A solution of 1,6-hexanediol (7.54 g, 63.80 mmol) in dry pyridine (2 ml) was treated dropwise with a solution of 3,4-methylenedioxybenzoyl chloride (PELTER *et al.*, 1982) (1.95 g, 10.56 mmol) in dry pyridine (10 ml). The mixture was stirred at room temperature for 15 min, then poured into ice, acidified with concentrated HCl up to $\text{pH}=1$ and extracted with diethyl ether (4×10 ml). The combined extracts were washed with water (2×20 ml), dried over anhydrous sodium sulphate, evaporated and crystallized at -60°C to afford ester **6** (2.40 g, 9.01 mmol; yield 85%; mp $31-33^{\circ}\text{C}$). IR (ν , cm^{-1}): 3430 (OH); 1715 (CO); 1486, 1242, 727. $^1\text{H-NMR}$ (δ , ppm): 1.47 (m, 8H), 3.62 (t, 2H), 4.28 (t, 2H), 6.00 (s, 2H), 6.78 (d, 1H), 7.40 (d, 1H), 7.58 (dd, 1H).

3,4-BIS[BENZYLOXY]BENZOYL CHLORIDE (**7**)

A mixture of 3,4-bis [benzyloxy] benzoic acid (SHIMIZU *et al.*, 1951) (2.50 g, 7.48 mmol), dry benzene (15 ml), oxalyl chloride (2.7 ml) and two drops of dry DMF was stirred at room temperature for 35 min, then it was evaporated at reduced pressure (0.01 Torr) to afford crude solid **7** [2.40 g, 6.80 mmol; yield 91%; mp 96°C (Lit. (PACHECO *et al.*, 1965) 96°C)].

1,6-HEXANEDIOL 1-(3,4-METHYLENEDIOXYBENZOATE) 6-(3,4-DIHYDROXYBENZOATE) (**9**)

A solution of **6** (1.12 g, 4.21 mmol) in dry pyridine (6 ml) was treated with solid **7** (1.78 g, 5.05 mmol) in small portions, stirred at room temperature for 10 min, poured into ice, acidified with concentrated HCl up to $\text{pH}=1$ and then extracted with diethyl ether

(4 × 25 ml). The extracts, washed with a saturated solution of sodium hydrogen carbonate, dried over anhydrous sodium sulphate and evaporated at reduced pressure were crystallized at -15 °C to afford 1,6-hexanediol 1-(3,4-methylenedioxybenzoate) 6-[3,4-bis(benzyloxy)benzoate] (**8**) (2.23 g, 3.83 mmol; yield 91%; mp 65 °C, isotropic transition 75 °C). IR (ν , cm^{-1}): 1680 (CO); 1490, 728. $^1\text{H-NMR}$ (δ , ppm): 1.50 (m, 4H), 1.78 (m, 4H), 4.30 (m, 4H), 5.20 (s, 2H), 5.22 (s, 2H), 6.00 (s, 2H), 6.83 (d, 1H), 6.93 (d, 1H), 7.41 (m, 1H), 7.67 (m, 3H). A mixture of **8** (1.78 g, 3.06 mmol), THF (13 ml) and glacial acetic acid (6 ml) was hydrogenated in a glass apparatus at room temperature in presence of 10% Pd/C (0.20 g) up to ceased hydrogen absorption (2h 15 min). Filtration of the catalyst and removal of the solvents at reduced pressure afforded **9** that was crystallized from acetonitrile (1.22 g, 3.03 mmol; yield 99%; mp 121 °C, isotropic transition 126 °C). IR (ν , cm^{-1}): 3490, 3310 (OH); 1698, 1670 (CO); 1486, 722. $^1\text{H-NMR}$ (DMSO-d_6 , δ , ppm): 1.46 (m, 4H), 1.72 (m, 4H), 4.23 (m, 4H), 6.13 (s, 2H), 6.83 (d, 1H), 7.02 (d, 1H), 7.37 (m, 3H), 7.60 (dd, 1H), 9.50 (broad, 2H). Mass spectrum, m/z (%): 402 (1, M^+).

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