NEW COMPOUNDS

Synthesis of Some New Aryl Phosphates

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Eight new triaryl phosphates (1–8) were synthesized by phosphorylation of the corresponding phenol with phosphorus oxychloride for evaluation as stationary phases in gas chromatography. They were duly characterized by infrared, proton magnetic resonance, and mass spectral techniques after their purity was established by HPLC.

Triaryl phosphates of the type $(RO)_3P{=}O$ (I) are synthesized by reaction of corresponding phenol with phosphorus oxychloride (*1*, *2*), orthophosphoric acid (*3*), or phosphorus pentachloride (*4*). Triaryl esters of the types $(RO)_2P(O)OR'$ (II) and $(R'O)(R''O)P(O)OR'''$ (III) are prepared stepwise by reaction of the corresponding sodium phenoxide or the phenol itself with a suitable aryl phosphoryl chloride (*5*, *6*). Multistage heating is generally followed during their synthesis (*7*, *8*). Tris(*p*-aminophenyl) phosphate was reported to have been obtained by nitration of triphenyl phosphate (*9*) followed by catalytic hydrogenation in the presence of Raney nickel (*10*).

We now report the synthesis and properties of eight new triaryl phosphates (Table I) of the types I (**1** and **2**; Scheme I) and II (**3–8**; Scheme II) by phosphorylation of the substituted phenols with phosphorus oxychloride following the multistep heating procedure required for successive displacement of the three chlorine atoms of the phosphorus oxychloride molecule. The compounds were synthesized with a view of evaluating them as suitable stationary phases in gas–liquid chromatography. The infrared absorptions (*11*, *12*), proton nuclear magnetic resonance absorptions (*13*), mass spectra (*14*), and liquid chromatographic behavior (*15*) of organophosphorus esters and related compounds have been reported.

Experimental Section

The IR spectra were recorded neat, unless otherwise stated, on a Perkin-Elmer 237B grating spectrophotometer, proton NMR on a Varian T-60 or Bruker-400 MHz spectrophotometer, and mass spectra on an AEI MS-30 spectrometer with an electron impact source. Varian 5020 HPLC was used to establish the purity of the products on reverse-phase column (MCH-10) with UV detector. Derivatograph MOM (OD103) Budapest was used for determining the thermal stability of the various phosphates from their TG and DTG curves following the method of Moskovskikh (*16*).

Phenol and *o*-cresol were distilled under reduced pressure, and 4-chloro-3-methylphenol was used as received. In each case the purity was checked by GC/HPLC. 2-Methoxy-4-*n*-propylphenol and 4-(2,3-dichloropropyl)phenol used in these preparations were obtained from eugenol as reported by us earlier (*17*).

Scheme I. Tris(2-methoxy-4-n-propylphenyl) Phosphate (1) and Tris(4-chloro-3-methylphenyl) Phosphate (2). Phosphorus oxychloride (0.097 mol) was slowly added from a dropping funnel to the corresponding phenol (0.3 mol) in a 250-mL round-bottom flask fitted with a condenser, mechanical stirrer, thermometer pocket, and a $CaCl_2$ guard tube. Continuous dry nitrogen purge under mild suction was used to remove the hydrogen chloride evolved in the reaction. Phosphorus pentachloride (ca. 0.5 g) was added to the reaction mixture, and the temperature was raised slowly by heating the flask in an oil bath. Trisubstitution required heating the reaction mixture in three stages, raising the temperature at each step only when evolution of hydrogen chloride ceased at the lower temperature. Thus, it was raised from 100 to 150 °C over a period of 3 h and then from 180 to 200 °C over 2 h. Compound **1** needed heating from 210 to 225 °C over 1.5 h while compound **2** required heating at 250–260 °C for 3 h for completion of the reaction.

Compound **1** was isolated by distillation of the reaction mixture under reduced pressure, in 63% yield, after a forerun of the starting phenol was neglected at 80 °C/0.3 mmHg.

In case of compound **2**, the reaction mixture was cooled and extracted with carbon tetrachloride (300 mL), and the extract was washed with 5% NaOH(aq) (3 × 100 mL) and water (until neutral). The extract was concentrated and compound **2** crystallized on the addition of a little methanol (yield 78%).

***Scheme II*: Step 1. Diphenyl Phosphorochloridate (A) and Bis(2-methylphenyl) Phosphorochloridate (B).** Phosphorus oxychloride (0.1 mol) was added very slowly to phenol (0.2 mol) containing *N*,*N*-dimethylaniline (10 drops), keeping the temperature below 40 °C, with the previously described experimental setup. The reaction mixture was heated at 100–130 °C for 10 h and for a further period of 6 h at 150–165 °C. Compound A was obtained, in 65% yield, by distillation: bp 141–143 °C/0.4 mmHg (Lit. (*7*) bp 172 °C/5 mmHg).

Compound B was similarly obtained, in 61% yield, from *o*-cresol without *N*,*N*-dimethylaniline and by heating the reaction mixture from 90 to 160 °C over a period of 6 h followed by distillation: bp 145–147 °C/0.4 mmHg.

***Scheme II*: Step 2. Triaryl Phosphates (3–8).** Triaryl phosphates (**3–5**) were prepared from diphenyl phosphorochloridate (A) and the esters (**6** and **8**) from bis(2-methylphenyl) phosphorochloridate (B) by heating slowly with the corresponding phenol in a slight excess of that required, raising the temperature from 130 to 180 °C until no more hydrogen chloride evolved (7–9 h). The ester (**7**) was prepared from B

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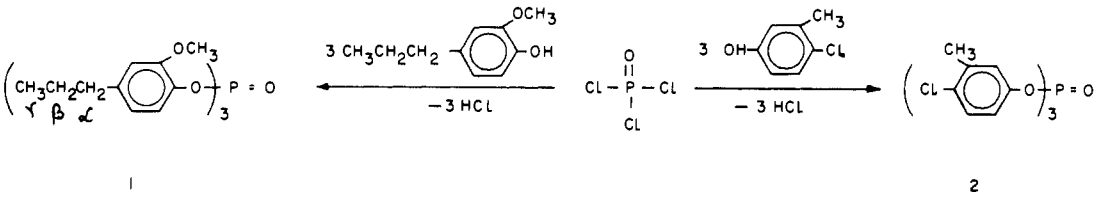
Table I. Properties of the Triaryl Phosphates

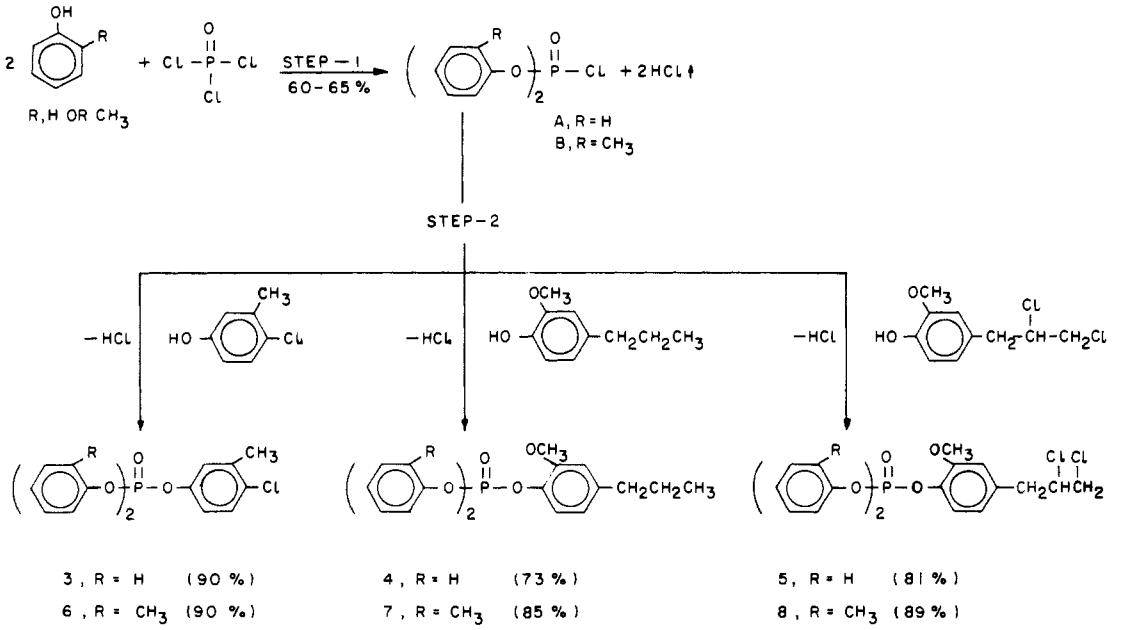
no.	compound	bp, °C/0.3–0.4 mmHg	IR, ν, cm^{-1}	^1H NMR,[a] ppm	m/e	DTG/ TG,[b] °C
1	tris(2-methoxy-4-*n*-propylphenyl) phosphate	257	1292, 1189, 960	6.37–7.12 (m, 9 H), 3.5 (s, 9 H), 2.17–2.40 (t, 6 H), 1.07–1.67 (m, 6 H), 0.55–0.78 (t, 9 H)	542 (M^+), 511, 496, 479, 465, 449, 436, 421, 391, 377, 362	230
2	tris(4-chloro-3-methylphenyl) phosphate	92[c]	1305,[d] 1150, 967, 715	6.83–7.28 (m, 9 H), 2.36 (s, 9 H)	470 (M^+), 435, 399, 345, 329, 311, 293, 266, 229, 213, 188, 142	255
3	diphenyl 4-chloro-3-methylphenyl phosphate	199–200	1293, 1180, 962, 640	6.73–6.88 (m, 13 H), 1.68 (s, 3 H)	374 (M^+), 339, 324, 281, 233, 170, 141, 107, 94	195
4	diphenyl 2-methoxy-4-*n*-propylphenyl phosphate	235–240	1308, 1294, 1183, 1018, 958	6.33–6.92 (m, 13 H), 3.41 (s, 3 H), 2.18–2.41 (t, 2 H), 1.10–1.70 (m, 2 H), 0.60–0.83 (t, 3 H)	398 (M^+), 383, 368, 355, 339, 325, 305, 281, 264, 251	190
5	diphenyl 2-methoxy-4-(2,3-dichloropropyl)-phenyl phosphate	252–254	1300, 1187, 1011, 963	7.11–7.37 (m, 10 H), 6.73–6.88 (m, 3 H), 4.22 (m, 1 H), 3.81–3.86 (m, 2 H), 3.73 (s, 3 H), 3.00–3.25 (m, 2 H)	466 (M^+), 430, 417, 369, 337, 325, 249	210
6	bis(2-methylphenyl) 4-chloro-3-methylphenyl phosphate	209–210	1302, 1162, 963, 635	7.25–7.35 (m, 3 H), 6.98–7.22 (m, 8 H), 2.32 (s, 3 H), 2.21 (s, 6 H)	402 (M^+), 387, 367, 352, 311, 295, 276, 261	195
7	bis(2-methylphenyl) 2-methoxy-4-*n*-propylphenyl phosphate	214–218	1306, 1166, 1040, 967	7.01–7.44 (m, 8 H), 6.64–6.71 (m, 3 H), 3.69 (s, 3 H), 2.51–2.55 (t, 2 H), 2.21 (s, 6 H), 1.55–1.65 (m, 2 H), 0.89–0.92 (t, 3 H)	426 (M^+), 412, 397, 383, 368, 319, 304	185
8	bis(2-methylphenyl) 2-methoxy-4-(2,3-dichloropropyl)phenyl phosphate	248–250	1291, 1156, 1030, 960, 750	7.06–7.43 (m, 8 H), 6.64–6.87 (m, 3 H), 4.21 (m, 1 H), 3.79–3.87 (m, 2 H), 3.70 (s, 3 H), 3.24–3.01 (m, 2 H), 2.20 (s, 6 H)	494 (M^+), 458, 445, 424, 397, 387, 351, 307, 291, 277	205

[a] NMR of compounds 1–4 in CCl_4, and 5–8 in $CDCl_3$. [b] Maximum temperature at which the compound starts losing weight. [c] Melting point. [d] IR in KBr pellet.

Scheme I. Type I Esters



Scheme II. Type II Esters



by heating in the temperature range of 160–210 °C over 6 h. Yields of the individual esters have been given in Scheme II. About 0.6 g of anhydrous $CaCl_2$ was added before the reaction for compounds **3**, **5**, **6**, and **8** was started.

Registry No. 1, 91785-84-1; 2, 91785-88-5; 3, 91785-85-2; 4, 91809-71-1; 5, 91809-72-2; 6, 91785-86-3; 7, 91809-70-0; 8, 91785-87-4; A, 2524-64-3; B, 6630-13-3; C_6H_5OH, 108-95-2; CH_3-o-C_6H_4-OH, 95-48-7; 4-chloro-3-methylphenol, 59-50-7; 2-methoxy-4-n-propylphenol, 2785-87-7; 4-(2,3-dichloropropyl)-2-methoxyphenol, 81480-43-5.

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Synthesis and Spectral Studies of Some Alkyl [(Substituted Phenylsulfonyl)methyl]benzoate Derivatives. 3

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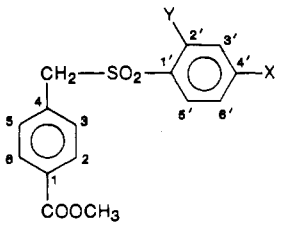
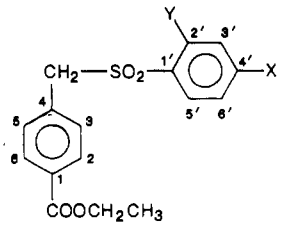
The synthesis, IR spectra, and proton NMR spectra of some alkyl [(substituted phenylsulfonyl)methyl]benzoate derivatives are reported.

As a continuation of our interest in substituted benzylphenyl sulfides and sulfones (*1-4*), a new series of methyl (**1a-h**) and ethyl (**2a-h**) [(substituted phenylsulfonyl)methyl]benzoates have been synthesized.



1

	X	Y
a	H	H
b	CH_3	H
c	OCH_3	H
d	NH_2	H



2

	X	Y
e	Cl	H
f	Br	H
g	NO_2	H
h	H	COOR

Experimental Section

Melting points are uncorrected. Infrared spectra (KBr pellets) were measured on a Pye Unicam Cambridge SP3-200 instrument and ^1H NMR spectra (acetone-d_6) on Varian XL200 with Me_4Si as internal standard. Elemental analyses were carried out in Cairo University, Egypt. The found elemental analysis data for carbon, hydrogen, and sulfur were in excellent agreement with those calculated.

General Procedure for the Synthesis of Methyl and Ethyl [(Substituted Phenylsulfonyl)methyl]benzoate. The sulfides and sulfones were prepared by previously reported procedures (*1*, *2*).

The sulfone esters **1a-h** and **2a-h** were synthesized by refluxing the corresponding acids in a mixture of absolute methyl or ethyl alcohol and a few drops of concentrated sulfuric acid for 10 h. The cooled reaction mixture was diluted with water and then washed with sodium bicarbonate solution. The solid products were recrystallized from dilute ethanol.

Methyl 4-[(Phenylsulfonyl)methyl]benzoate (1a). White crystals: yield 86%; mp 60-1 °C; ^1H NMR δ 3.92 (s, methyl ester group, 3 H), 4.68 (s, CH_2, 2 H), 7.85 (d, C_2 and C_6, 2 H), 7.48 (d, C_3 and C_5, 2 H), 7.64 (d, C_2' and C_6', 2 H), 7.51 (t, C_3', C_4', and C_5', 3 H).

Methyl 4-[(4'-Tolylsulfonyl)methyl]benzoate (1b). White solid: yield 83%; mp 156-7 °C; ^1H NMR δ 2.45 (s, CH_3, 3 H), 3.90 (s, methyl ester group, 3 H), 4.65 (s, CH_2, 2 H), 7.98 (d, C_2 and C_6, 2 H), 7.35 (d, C_3 and C_5, 2 H), 7.58 (d, C_2' and C_6', 2 H), 7.25 (d, C_3' and C_5', 2 H).

Methyl 4-[((4'-Methoxyphenyl)sulfonyl)methyl]benzoate (1c). White solid: yield 81%; mp 145-7 °C; ^1H NMR δ 3.85 (s, OCH_3, 3 H), 3.90 (s, methyl ester group, 3 H), 4.58 (s, CH_2, 2 H), 7.92 (d, C_2 and C_6, 2 H), 7.03 (d, C_3 and C_5, 2 H), 7.60 (d, C_2' and C_6', 2 H), 7.35 (d, C_3' and C_5', 2 H).

Methyl 4-[((4'-Aminophenyl)sulfonyl)methyl]benzoate (1d). Yellow solid: yield 76%; mp 175-6 °C; ^1H NMR δ 3.90 (s, methyl ester group, 3 H), 4.48 (s, NH_2, 2 H), 4.82 (s, CH_2, 2 H), 8.20 (d, C_2 and C_6, 2 H), 7.88 (d, C_3 and C_5, 2 H), 8.00 (d, C_2' and C_6', 2 H), 7.37 (d, C_3' and C_5', 2 H).

Methyl 4-[((4'-Chlorophenyl)sulfonyl)methyl]benzoate (1e). White crystals: yield 91%; mp 134-5 °C; ^1H NMR δ 3.82 (s, methyl ester group, 3 H), 4.70 (s, CH_2, 2 H), 7.81 (d, C_2 and C_6, 2 H), 7.19 (d, C_3 and C_5, 2 H), 7.72 (d, C_3' and C_5', 2 H), 7.57 (d, C_2' and C_6', 2 H).

Methyl 4-[((4'-Bromophenyl)sulfonyl)methyl]benzoate (1f). White solid: yield 94%; mp 152-4 °C; ^1H NMR δ 3.78 (s, methyl ester group, 3 H), 4.73 (s, CH_2, 2 H), 7.85 (d, C_2 and C_6, 2 H), 7.25 (d, C_3 and C_5, 2 H), 7.58 (d, C_2' and C_6', 2 H), 7.76 (d, C_3' and C_5', 2 H).

Methyl 4-[((4'-Nitrophenyl)sulfonyl)methyl]benzoate (1g). Yellow solid: yield 96%; mp 181-2 °C; ^1H NMR δ 3.86 (s, methyl ester group, 3 H), 4.92 (s, CH_2, 2 H), 8.22 (d, C_2 and C_6, 2 H), 7.38 (d, C_3 and C_5, 2 H), 7.90 (d, C_2' and C_6', 2 H), 7.98 (d, C_3' and C_5', 2 H).

Methyl 4-[((2'-Carbomethoxyphenyl)sulfonyl)methyl]-benzoate (1h). White solid: yield 82%; mp 148-9 °C; ^1H

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