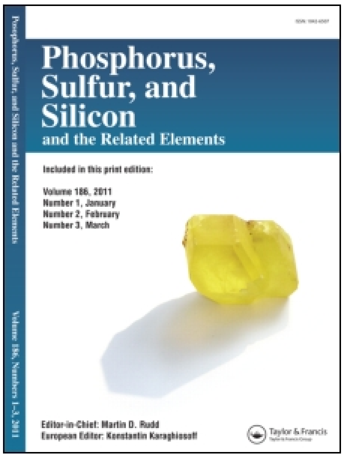

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SYNTHESIS OF SOME PHOSPHORUS DERIVATIVES OF CARDANOL

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SYNTHESIS OF SOME PHOSPHORUS DERIVATIVES OF CARDANOL

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The synthesis of some phosphonates obtained by reaction of cardanol and 3-n-pentadecylphenol with pentavalent phosphorus chlorides containing oxygen or sulfur atom is reported.

INTRODUCTION

"Cashew nut shell liquid" (CNSL) is an interesting oil contained in the shell of the cashew nut (*Anacardium occidentale*). This oil derives in part as side-product from the mechanical methods of the cashew nut process in view of the high edible use of the kernel, and represents a low cost, widely available and versatile alternative raw material for several chemical applications.[1,2]

Especially during the last twenty years the chemistry and industrial utilization of CNSL, its components, and their derivatives have been intensively investigated. However, the phosphorus derivatives of these compounds appear to be much less studied than other derivatives, in spite of their considerable industrial interest in particular as additives for lubricants.[3]

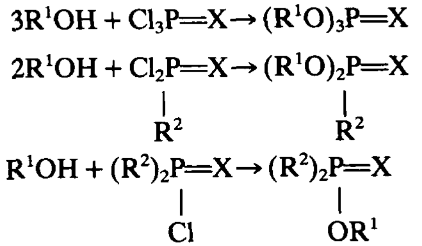
Considering also the fairly good availability of an highly pure and long time stable cardanol (called Stabilcardo^{R}) recently produced by a pilot plant from CNSL in semi-industrial scale, the studies mentioned above seem to be particularly attractive and appropriate.[2,4]

RESULTS AND DISCUSSION

In this paper we report the synthesis of some phosphonates (**3a–n**) prepared by reaction of cardanol and 3-n-pentadecylphenol (**1**) with pentavalent phosphorus chlorides containing oxygen or sulfur (**2**).

These reactions occur under mild conditions, providing the products in good yields without complicated reaction procedures and manipulations.

All the above-mentioned compounds have a very good solubility in mineral lubricating oil. At present, the tests on the lubricants containing these products as additives are in progress.



$$3R^1OH + Cl_3P{=}X \rightarrow (R^1O)_3P{=}X$$

$$2R^1OH + Cl_2\underset{R^2}{\underset{|}{P}}{=}X \rightarrow (R^1O)_2\underset{R^2}{\underset{|}{P}}{=}X$$

$$R^1OH + (R^2)_2\underset{Cl}{\underset{|}{P}}{=}X \rightarrow (R^2)_2\underset{OR^1}{\underset{|}{P}}{=}X$$

1 **2** **3**

$R^1 = 3\text{-}C_{15}H_{25-31}C_6H_4$; $3\text{-}C_{15}H_{31}C_6H_4$

$R^2 = CH_3$; C_2H_5

X = O, S

SCHEME

TABLE I

Reaction times and spectral data of products 3

Product	R^1	R^2	X	Time (h)	Ir(neat) ν (cm^{-1})	^{1}H nmr(CCl$_4$/TMS$_{int}$)[a] δ (ppm)
3a	$3\text{-}C_{15}H_{25-31}C_6H_4$		O	3	3010, 2930, 1590, 1300, 1230, 985	a
3b	$3\text{-}C_{15}H_{31}C_6H_4$		O	3	2930, 1590, 1300, 1230, 985	a
3c	$3\text{-}C_{15}H_{25-31}C_6H_4$		S	3	3015, 2930, 1590, 1230, 975	a
3d	$3\text{-}C_{15}H_{31}C_6H_4$		S	3	2930, 1585, 1225, 975	a
3e	$3\text{-}C_{15}H_{25-31}C_6H_4$	CH_3	O	1	3015, 2930, 1590, 1315, 1240, 1150, 970	1.65(d, J_{PCH} 18 Hz, CH$_3$)[a]
3f	$3\text{-}C_{15}H_{31}C_6H_4$	CH_3	O	1	2930, 1590, 1310, 1240, 1155, 970	1.65(d, J_{PCH} 18 Hz, CH$_3$)[a]
3g	$3\text{-}C_{15}H_{25-31}C_6H_4$	CH_3	S	3	3015, 2930, 1590, 1300, 1230, 1140, 965	2.09(d, J_{PCH} 14 Hz, CH$_3$)[a]
3h	$3\text{-}C_{15}H_{31}C_6H_4$	CH_3	S	3	2930, 1590, 1300, 1230, 1145, 970	2.41(d, J_{PCH} 14 Hz, Cl$_3$)[a]
3i	$3\text{-}C_{15}H_{25-31}C_6H_4$	OCH_3	S	18	3015, 2930, 1590, 1240, 1040, 975, 835	3.86(d, J_{PCH} 13 Hz, OCH$_3$)[a]
3j	$3\text{-}C_{15}H_{31}C_6H_4$	OCH_3	S	18	2930, 1590, 1240, 1045, 975, 835	3.83(d, J_{PCH} 12 Hz, OCH$_3$)[a]
3k	$3\text{-}C_{15}H_{25-31}C_6H_4$	OC_2H_5	O	3	3015, 2930, 1590, 1270, 1245, 1035, 980	1.2–1.7 (m, OEt), 3.8–4.3 (m, OEt)[a]
3l	$3\text{-}C_{15}H_{31}C_6H_4$	OC_2H_5	O	3	2930, 1590, 1280,. 1245, 1035, 980	1.1–1.6 (m, OEt), 3.8–4.4 (m, OEt)[a]
3m	$3\text{-}C_{15}H_{25-31}C_6H_4$	OC_2H_5	S	18	3015, 2930, 1590, 1240, 1030, 970	1.05–1.6 (m, OEta), 3.9–4.5 (m, OEt)[a]
3n	$3\text{-}C_{15}H_{31}C_6H_4$	OC_2H_5	S	18	2930, 1590, 1240, 1030, 975	1.07–1.65 (m, OEt), 3.9–4.5 (m, OEt)[a]

[a] In addition to those reported in Table, all the compounds obtained showed the signals reported in the note 4 or 5 relative to cardanol and 3-n-pentadecylphenol, respectively, with the exception of the signal at $\delta = 6.08$ ppm ascribable to the OH proton.

EXPERIMENTAL

Cardanol was kindly supplied by OLTREMARE S.p.A. (Bologna, Italy) with the commercial name of STABILCARDO^{R}.[2,4] 3-n-Pentadecylphenol, obtained by catalytic hydrogenation of STABILCARDO^{R}, was also kindly supplied by OLTREMARE S.p.A.[2,4,5] Phosphorus chloride derivatives were commercial materials and were used without further purification. Ir and ^{1}H nmr spectra were recorded on a Perkin-Elmer 298 and a Varian EM-360L spectrometer at 60 MHz, respectively. The ν and δ values of characteristic peaks are summarized in Table I. All the compounds obtained showed a satisfactory elemental analysis.

Preparation of Compounds **3a–n**. *General Procedure.* Cardanol or 3-n-pentadecylphenol (**1**, 3 mmol), sodium hydroxide (1.2 equiv. with respect to **1**), and phosphorus chlorides (**2**, 1.2 equiv. for phosphorus monochloride derivatives, 0.6 equiv. for phosphorus dichloride derivatives, and 0.4 equiv. for phosphorus trichloride derivatives with respect to **1**) were dissolved in methylene chloride (20 ml). The mixture was heated under reflux during 3–18 h until the reaction was complete (monitored by t.l.c. on silica gel). The mixture was poured into a separatory funnel, washed with 10% aqueous sulfuric acid, and then with water. The organic phase was separated, dried with anhydrous sodium sulfate, and evaporated under reduced pressure, to afford oily product (**3**) in satisfactory purity and good yields (90–95%). Further purification may be obtained by chromatography on a silica gel column or by distillation under reduced pressure. In the case of the synthesis of **3e** and **3f**, sodium hydroxyde was substituted with sodium hydride that was slowly (30 min) added to the reaction mixture at room temperature under mechanical stirring until the reaction was complete (1 h). Afterward the reaction was work up as described above in detail.

ACKNOWLEDGMENT

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2. O. Attanasi (OLTREMARE S.p.A.), Ital. Pat. n. 12458 A/79, 9.2.1979.
3. G. J. J. Jayne, R. I. Barber and J. S. Elliot, (E. Cooper and Co. Ltd) Brit. 1,254,554, 24 Nov 1971.
4. The long chain of cardanol may be saturated, monolefinic (8), diolefinic (8, 11), and triolefinic (8, 11, 14), with an average value of 2 double bond per molecule. ^{1}H nmr (CCl_4/TMS_{int}): δ 0.9 (s, Me), 1.33 (s, CH_2), 1.8–2.32 (m, allyl), 2.33–2.66 (m, benzyl), 2.67–3.0 (m, diallyl), 5.2–5.6 (m, vinyl), 6.08 (s broad, OH, D_2O exchange), 6.5–7.5 (m, aryl) ppm.
5. 3-n-Pentadecylphenol. ^{1}H nmr (CCl_4/TMS_{int}): δ 0.95 (s, Me), 1.36 (s, CH_2), 2.32–2.68 (m, benzyl), 6.07 (s broad, OH, D_2O exchange), 6.49–7.58 (m, aryl) ppm.