REACTION OF DIALKYLPHOSPHOROUS ACIDS WITH STERICALLY HINDERED BENZOQUINONIMINES

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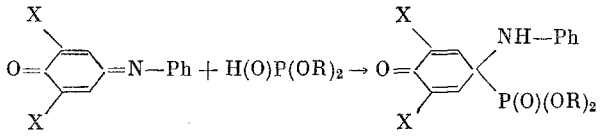
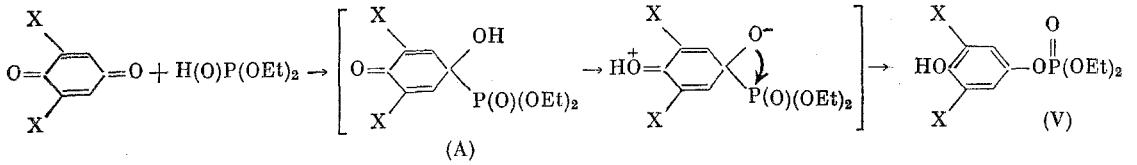
Arbuzov et al. [1] reported that dialkylphosphorus acids react with quinones to form 1,6-addition products. We studied the reaction of dialkylphosphorous acids with the 1-phenylimine of 2,5-di-tert-butyl-4-benzoquinone and found that the addition proceeds at the C=N bond



where R = Me (I), Et (II), Bu (III), C_6H_{13} (IV) and X = t-Bu, to form O,O-dialkyl-1-phenylamino-3,5-di-tert-butyl-4-benzoquinol-1-phosphonates, which are lightly colored products crystallizable from aqueous methanol or hexane. The IR spectra of these products show bands at 1235-1245 (P=O), 1665-1670 (C=O), 1510-1610 (C=C), and 3295-3330 cm^{-1} (NH). The lack of the band at 3600-3630 cm^{-1} characteristic for the phenol hydroxyl group [2] supports the quinolide structure. The ^{31}P NMR spectra display signals at 18-24 characteristic for O,O-dialkylalkylphosphonates [3]. The physicochemical indices of these products are given in Table 1.

For comparison, we carried out the reaction of diethylphosphorous acid with 2,6-di-tert-butyl-4,6-benzoquinone, which proceeds by 1,6-addition to form diethyl-3,5-di-tert-butyl-4-hydroxyphenyl phosphate (V) as the major product



(A)

Cyclohexadiene structure (A) is apparently converted to aromatic species (V) by the phosphonate—phosphate rearrangement found for α-hydroxyalkylphosphonates [4]. On the other hand, the behavior of alkylated benzoquinonimines in their reaction with dialkylphosphorous acids is largely a consequence of the high stability of the quinolide structure having a phenylamino group in the α-position relative to the phosphorous atom.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer. The ^{31}P NMR spectra were taken on a KGU-4 spectrometer at 10.2 MHz from 85% H_3PO_4. A sample of 3,5-di-tert-butyl-4-benzoquinone 1-phenylimine was obtained from 2,6-di-tert-butyl-1,4-benzoquinone and aniline by heating at reflux in toluene with removal of the water formed by azeotropic distillation.

Reaction of O,O-Diethylphosphorous Acid with 3,5-di-tert-butyl-4-benzoquinone 1-phenylimine. A mixture of 3 g (0.01 mole) quinonimine and 1.5 g (0.011 mole) diethylphosphorous acid in the presence of $Et_2O \cdot BF_3$ was maintained for 24 h at 25-30°C. The crystals formed were recrystallized from 3:1 methanol—water to yield 3.3 g (75.6%) O,O-diethyl-1-phenylamino-3,5-di-tert-butyl-4-benzoquinol-1-phosphonate (II) with mp 111.6-113°C.

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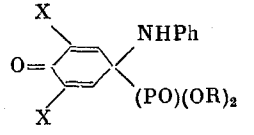
TABLE 1. O,O-Dialkyl-1-phenylamino-3,5-di-tert-butyl-4-benzoquinol-1-phosphonates 

Compound	R	Yield, %	bp, °C	Found, %				Chemical formula	Calculated, %				$\delta^{31}P$, ppm
				C	H	N	P		C	H	N	P	
(I)	Me	46,5	121–123,5	65,38	7,87	3,61	7,80	$C_{22}H_{32}NO_4P$	65,16	7,95	3,45	7,62	24
(II)	Et	75,6	111,6–113	66,32	8,49	4,20	7,62	$C_{24}H_{36}NO_4P$	66,45	8,39	3,74	7,15	18
(III)	Bu	48,7	98–99	68,47	8,69	2,80	7,20	$C_{28}H_{44}NO_4P$	68,69	9,07	2,86	6,33	22
(IV)	C_6H_{13}	65,2	Viscous liquid	70,82	9,71	2,38	5,77	$C_{32}H_{52}NO_4P$	70,42	9,60	2,56	5,68	

Note: IR spectra (ν, cm^{-1}): (II) 1240 (P=O), 1510 and 1610 (C=C), 1665 (C=O), 3295 (NHR); in CCl_4: 1265 (P=O), 1510 and 1610 (C=C), 1665 (C=O), 3300 (NHR); (III): 1240 (P=O), 1510 and 1610 (C=C), 1670 (C=O), 3300 (NHR); in CCl_4: 1245 (P=O), 1510 and 1610 (C=C), 1665 (C=O) and 3300 (NHR).

Analogous procedures yielded O,O-dimethyl- (I), O,O-dibutyl- (III), and O,O-dihexyl-1-phenylamino-3,5-di-tert-butyl-4-benzoquinol-1-phosphonates (see Table 1).

Reaction of 3,5-Di-tert-butyl-1,4-benzoquinone with Diethylphosphorous Acid. A mixture of 2.2 g (0.01 mole) quinone and 1.5 g (0.011 mole) diethylphosphorous acid in the presence of sodium ethylate was maintained for 20 h at 30°C. Then, 20 ml benzene was added to the mixture, and the solution was washed with aqueous sodium carbonate and dried over $MgSO_4$. Benzene was evaporated in vacuum, and the product was recrystallized twice from hexane to yield 3.1 g (85%) (V), mp 77-78°C. Found, %: C 60.58; H 8.66; P 8.56. $C_{28}H_{31}O_5P$. Calculated, %: C 60.30; H 8.71; P 8.64. IR spectrum (ν, cm^{-1}): 1275 (P=O), 1596 ($C=C_{arom}$), 3330 (phenol OH). ^{31}P NMR spectrum: −13 ppm [13].

CONCLUSIONS

1. Dialkylphosphorous acids in the presence of $Et_2O \cdot BF_3$ add to the 1-phenylimine of 3,5-di-tert-butyl-4-benzoquinone at the C=N bond to form dialkyl α-aminoquinolphosphonates.

2. Diethylphosphorous acid reacts with 3,5-di-tert-butyl-1,4-benzoquinone to give O,O-diethyl-3,5-di-tert-butyl-4-hydroxyphenyl phosphate.

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