for 30 min, the reaction mixture was basified with ammonia and extracted with $CHCl_3$. The extract was washed with 10% NaOH in order to separate the products into nonphenolic and phenolic fractions. Purification of the nonphenolic material by tlc (silica, using 1:1 benzene–acetone as developer) gave 9-benzyloxy-1,2,10-trimethoxydibenz[*de*,*g*]quinolin-7-one (XVI, 47 mg): mp 228° dec ($CHCl_3$–MeOH); ir (KBr) 5.95 (CO), 13.60, 14.45 μ (monosubstituted benzene); nmr δ 8.82 (1 H, d, J = 6.0 Hz, C_5 H), 8.73 (1 H, s, C_{11} H), 8.06 (1 H, s, C_8 H), 7.68 (1 H, d, J = 6.0 Hz, C_4 H), 7.60–7.25 (5 H, m, C_6H_5), 7.12 (1 H, s, C_3 H), 5.30 (2 H, s, OCH_2Ph), 4.07, 4.03, 4.00 (each 3 H, s, 3 OCH_3); uv λ_{max}^{EtOH} 243 nm (log ε 4.04), 272 (4.03), 291 (sh, 3.85), 355 (3.65), 380 (sh, 5.95), 428 (sh, 3.45); mass spectrum m/e 427 (M^+), 336, 91 (tropylium ion).

Anal. Calcd for $C_{26}H_{21}NO_5$: C, 73.05; H, 4.95; N, 3.28. Found: C, 72.55; H, 4.84; N, 3.28.

The aqueous alkaline layer was neutralized with ammonium chloride and then extracted with $CHCl_3$. The extract was dried over sodium sulfate. The usual work-up gave a brownish gum, which was purified by tlc (silica, using 10:1 $CHCl_3$–MeOH as developer) to give 9-hydroxy-1,2,10-trimethoxydibenz[*de*,*g*]-quinolin-7-one (II, 6 mg) as an amorphous powder: mp 252° dec ($CHCl_3$–*n*-hexane); ir (KBr) 2.93 (OH), 6.00 μ (CO); uv λ_{max}^{EtOH} 243 nm (log ε 4.12), 273 (4.11), 292 (3.92), 354 (3.70), 380 (sh), (3.67), 435 (3.55); $\lambda_{max}^{EtOH-NaOH}$ 251 nm (log ε 4.07), 296 (3.99), 324 (3.97), 390 (3.42), 535 (3.30); $\lambda_{max}^{EtOH-HCl}$ 256 nm (log ε 4.08), 286 (4.01), 380 (3.68), 500 (3.17); mass spectrum m/e 337 (M^+).

Hydrolysis of XIX.—A mixture of *O*-benzylatheroline (XVI, 22 mg), tetrahydrofuran (3 ml), and hydrochloric acid (5 ml) was refluxed for 2 hr. The solvent was evaporated to afford a dark purple hydrochloride, which was washed with ether, suspended in $CHCl_3$, and basified with ammonia. The $CHCl_3$ extract was dried (Na_2SO_4) and the solvent was then concentrated to 5 ml. Addition of a small amount of *n*-hexane gave atheroline (II, 11 mg) as an amorphous yellow powder, mp 252° dec.

9-Acetoxy-1,2,10-trimethoxydibenz[*de*,*g*]quinolin-7-one (III).—A mixture of synthetic atheroline (II, 10 mg), tetrahydrofuran (15 ml), acetic anhydride (10 drops), and potassium carbonate (300 mg) was stirred for 20 hr at room temperature. The inorganic salt was filtered off and the solvent was then evaporated to give a gum which was extracted into $CHCl_3$. The extract was washed with 5% $NaHCO_3$ and water and dried (Na_2SO_4), and the solvent was evaporated. Trituration with ether gave crystals which were recrystallized ($CHCl_3$–ether) to give 9-acetoxy-1,2,10-trimethoxydibenz[*de*,*g*]quinolin-7-one (III) (9 mg) as yellow needles: mp 216–218° dec; ir (KBr) 5.54 ($OCOCH_3$), 5.92 μ (CO); nmr ($CDCl_3$) δ 8.82 (1 H, s, C_{11} H), 8.82 (1 H, d, J = 6.0 Hz, C_5 H), 8.20 (1 H, s, C_8 H), 7.68 (1 H, d, J = 6.0 Hz, C_4 H), 7.14 (1 H, s, C_3 H), 4.04 (3 H, s, OCH_3), 4.02 (6 H, s, 2 OCH_3), 2.37 (3 H, s, $OCOCH_3$); nmr (CF_3COOH) δ 9.08 (1 H, s, C_{11} H), 8.73 (1 H, d, J = 6.0 Hz, C_5 H), 8.50 (1 H, d, J = 6.0 Hz, C_4 H), 8.26 (1 H, s, C_8 H), 7.68 (1 H, s, C_3 H), 4.37, 4.31, 4.18 (each 3 H, s, 3 OCH_3), 2.50 ppm (3 s, H, $OCOCH_3$). Its spectral properties (ir, nmr) were identical with those of *O*-acetylatheroline derived from natural atheroline, and a mixture melting point (216–219° dec) showed no depression.[9]

Registry No.—II, 1349-20-8; III, 5140-36-3; VI, 35096-38-9; VII, 35096-39-0; X, 35096-40-3; XI, 35096-42-5; XIII, 35096-41-4; XIV, 35096-43-6; XVI, 35096-44-7.

Acknowledgment.—We are grateful to Professor I. R. C. Bick for a generous sample of *O*-acetylatheroline. We also thank the National Institutes of Health for a grant (CA 11445) in support of this work.

Reduction and Hydrolysis of Triethyl α-Phosphonocinnamate and Its Derivatives

CHARLES N. ROBINSON,* PHILIP K. LI, AND JOHN F. ADDISON[1]

Department of Chemistry, Memphis State University, Memphis, Tennessee 38111

Received February 3, 1972

The triethyl ester of α-phosphonocinnamic acid and some of its derivatives can be reduced with sodium borohydride to the corresponding triethyl α-phosphonohydrocinnamates. Hydrolysis of both the unsaturated and the saturated esters in concentrated hydrochloric acid causes dephosphonation and the formation of cinnamic acid and hydrocinnamic acid and their derivatives, respectively.

A number of aromatic aldehydes, **1**, undergo condensation with triethyl phosphonoacetate (**2**) to give triethyl α-phosphonocinnamates (**3**)[2] (Scheme I); however, the chemistry of compounds of type **3** has been examined only cursorily to date. As a part of an attempt to find a convenient general method for the synthesis of β-styryl- (**10**) and β-phenethylphosphonic acids[3] (**11**), we have examined some of the chemical properties of these compounds.

Reduction.—The selective reduction of the carbon–carbon double bond of the phosphonocinnamate esters **3** to give the corresponding phosphonopropionates **4** has been accomplished by treating the unsaturated esters with a 1:1 molar ratio of $NaBH_4$.[4] The results of these reductions are summarized in Table I. Both ethanol and pyridine were used as solvents; it may be deduced from Table I that pyridine is the superior solvent. The reduction reactions were relatively simple to carry out; however, some decomposition occurred during distillation and considerable difficulty was experienced in obtaining analytically pure products. Due to the minor differences in the percentage composition of starting materials and products, more emphasis was placed on nmr data than on elemental analysis. In the case of the unsaturated esters **3**, absorption due to the vinylic hydrogen occurred as a doublet (J = 24 ± 1 cps) at δ 7.52–8.42; in the reduced esters **4**, the absorption in this region disappeared with the emergence of new absorption at δ 2.7–3.3 (multiplet) due to the new methylene and methine hydrogens.

In addition to the compounds listed in Table I, attempts were made to reduce three other compounds: triethyl *p*-methyl-α-phosphonocinnamate, triethyl 3,4-dimethoxy-α-phosphonocinnamate, and the diethyl ester of courmarin-3-phosphonic acid (**15**). Decomposition during distillation of the reduced products was so extensive that reasonable analyses could not be obtained; however, the vinylic proton absorption in the nmr spectra of the crude products was reduced in size or disappeared entirely and the expected absorption appeared in the δ 2.7–3.3 region. Additional evidence for

(1) (a) The authors gratefully acknowledge the support of this work by the National Institutes of Health, U. S. Public Health Service (GM-12480). (b) Part of the work discussed in this article is abstracted from work presented for the M.S. Thesis by P. K. Li.

(2) C. N. Robinson and J. F. Addison, *J. Org. Chem.*, **31**, 4825 (1966).

(3) This problem has now largely been solved by the work of G. H. Jones, E. K. Hamamura, and J. G. Moffatt, *Tetrahedron Lett.*, 5731 (1968).

(4) Reduction procedures were patterned after the work of S. B. Kadin, *J. Org. Chem.*, **31**, 620 (1966).

SCHEME I

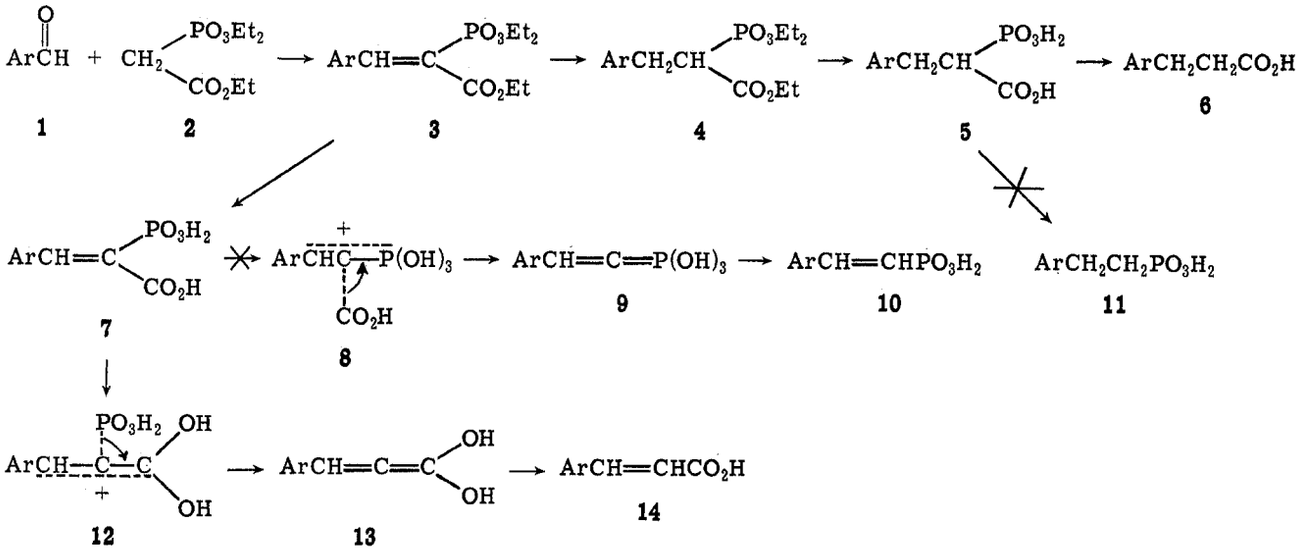
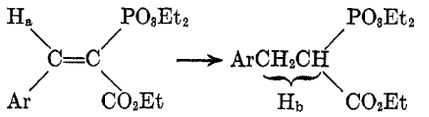


TABLE I

REDUCTION OF TRIETHYL α-PHOSPHONOCINNAMATES



Registry no.	No.	Aryl group	Product bp, °C (mm)	Yield, %	Formula	Anal., % Calcd P	Anal., % Found P	Nmr, δ H_a	Nmr, δ H_b, estd[a]
35085-32-6	1	C_6H_5	145–149 (0.35)	70[b]	$C_{15}H_{23}O_5P$			7.60	3.12
			189–191 (5.00)	70[c]		9.86	9.86		
35085-33-7	2	p-$CH_3OC_6H_4$	134–137 (0.30)	83[b]	$C_{16}H_{25}O_6P$	9.00	9.10	7.52	2.70
			122–124 (0.05)	71[c]					
35085-34-8	3	p-ClC_6H_4	166–167 (0.30)	74[b]	$C_{15}H_{22}O_5PCl$	8.88	8.74	7.52	3.19
			151–153 (0.15)	70[c]			8.72		
35085-35-9	4	1-$C_{10}H_7$	124–126 (0.05)	52[b]	$C_{19}H_{25}O_5P$	8.50	8.71	8.41	3.30
			131–134 (0.10)	34[c]					

[a] The multiplet for the methylene and methine protons represent the ABC portion of an ABCX pattern and the chemical shift shown is an estimate of the center of the ABC portion. [b] Pyridine as the solvent. [c] Ethanol as the solvent.

the reduction of the coumarin derivative is presented below.

Hydrolysis of Unsaturated Esters.—In 1960 Patai and Schwartz[5] reported that hydrolysis of triethyl α-phosphonocinnamate under a variety of conditions gave only cinnamic acid (**14**), contrary to the original report of Pudovik and Lebedeva[6] that α-phosphonocinnamic acid (**7**) was formed. We have previously reported[2] that the hydrolysis of **15** gave reasonably good yields of coumarin-3-phosphonic acid (**16**) (Scheme II), which lost the phosphonic acid group with difficulty (at >250°) to produce coumarin (**21**). This indicated that there was a possibility, however slight, that varying the substituent attached to the aromatic ring might alter the course of the reaction. The C–C bond and the C–P bond are reported to be of about equal strength[5] and, if decarboxylation rather than dephosphonation could be effected, the desired β-styrylphosphonic acids (**10**) would be produced.

Several of these unsaturated esters (Table II, type A) were therefore hydrolyzed, but in each case only the dephosphonated product was formed. Evidently, substitution may affect the stability of the phosphonic acid but not the course of the reaction. Two possible reasons can be advanced for dephosphonation in preference to decarboxylation. In the protonation of the phosphonic acids **7**, transition state **12** would be more stable than **8** because of the poor p–d overlap required for resonance stabilization in **8**. Also, in the completed decomposition, **13** would be more stable than **9** for the same reason. The stability of the coumarin-3-phosphonic acid (**16**), on the other hand, is enhanced by the fact that the protonated acid, **17** ↔ **18**, probably cannot lose the phosphono group directly to give the unstable enol **19**, which would be an angular allene. A more likely route for this more difficult decomposition involves either tautomerization of the protonated acid to **20** or direct protonation of the double bond.

As mentioned earlier, **15** was also reduced with $NaBH_4$ and, although the intermediate ester, **22**, could not be purified for analysis, the hydrolysis of the crude product resulted in dephosphonation and the formation of 3,4-dihydrocoumarin (**26**). In this case there is no steric inhibition to formation of **25** such as exists for the formation of **19**.

(5) S. Patai and A. Schwartz, *J. Org. Chem.*, **25**, 1232 (1960).

(6) A. N. Pudovik and N. M. Lebedeva, *Dokl. Akad. Nauk SSSR*, **90**, 799 (1953); *Chem. Abstr.*, **50**, 2429d (1956).

SCHEME II

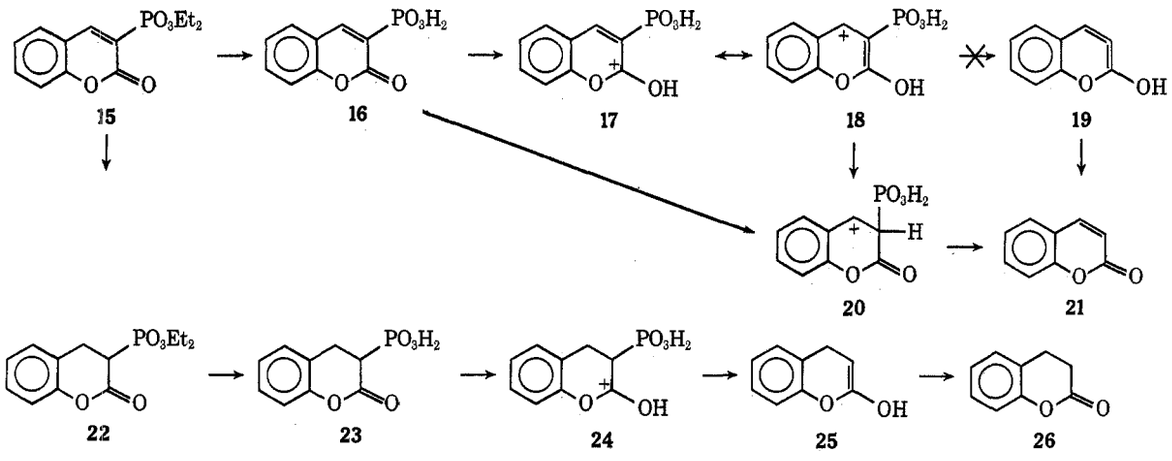


TABLE II

HYDROLYSIS OF ESTERS

No.	Aryl group	Product mp, °C	Reported mp, °C
Type A	$ArCH{=}C(PO_3Et_2)(CO_2Et) \longrightarrow ArCH{=}CHCO_2H$		
1	C_6H_5	134–135	132–134[a]
2	p-$CH_3C_6H_4$	198–202	199[b]
3	p-$CH_3OC_6H_4$	170	174[b]
4	p-ClC_6H_4	237–240	241[c]
5	1-$C_{10}H_7$	208–210	209–212[d]
Type B	$ArCH_2CH(PO_3Et_2)(CO_2Et) \longrightarrow ArCH_2CH_2CO_2H$		
6	C_6H_5	47–48	49[e]
7	p-ClC_6H_4	123	125[f]

[a] C. F. Koelsch, *J. Amer. Chem. Soc.*, **65**, 57 (1943). [b] J. F. J. Dippy and J. E. Page, *J. Chem. Soc.*, 362 (1938). [c] J. v. Braun and J. Nelles, *Chem. Ber.*, **66**, 1467 (1933). [d] B. L. West, *J. Amer. Chem. Soc.*, **42**, 1664 (1920). [e] K. Kindler and W. Peschke, *Justus Liebigs Ann. Chem.*, **497**, 196 (1932). [f] K. Kindler and T. Li, *Chem. Ber.*, **74**, 321 (1941).

Arbusov and Razumov[7] have prepared triethyl α-phosphonohydrocinnamate (**4**) (unsubstituted) by the benzylation of triethyl phosphonoacetate (**2**), and hydrolyzed the product with HCl in a sealed tube at 150° to produce α-phosphonohydrocinnamic acid (**5**). We have hydrolyzed this ester and its *p*-chloro derivative (Table II, type B) with concentrated hydrochloric acid at atmospheric pressure and, as would be expected, obtained the dephosphonated products **6**, but none of the decarboxylation products, **11**.

(7) A. E. Arbusov and A. I. Razumov, *J. Russ. Phys. Chem. Soc.*, **61**, 623 (1929).

Experimental Section

The triethyl α-phosphonocinnamates were prepared by the method of Robinson and Addison.[2] Melting points (uncorrected) were obtained on a Fisher-Johns melting point apparatus. Analyses were by M-H-W Laboratories, Garden City, Mich. Nmr spectra were taken in deuteriochloroform with tetramethylsilane as an internal standard, using a Varian HA-60 spectrometer.

All of the reductions listed in Table I were carried out in essentially the same manner illustrated by procedures 1 and 2 below. The hydrolysis reactions referred to in Table II were conducted according to procedure 3 below.

Procedure 1. Reduction of Triethyl α-Phosphonocinnamate in Pyridine.—A solution of 1.9 g (0.05 mol) of $NaBH_4$ in 30 ml of cold, dry pyridine was added dropwise to a mixture of 15.6 g (0.05 mol) of triethyl α-phosphonocinnamate and dry pyridine at 0–5°. This mixture foamed vigorously and changed from light brown to colorless. After the addition was complete, the mixture was stirred at 0–5° for 1 hr and at room temperature for 1 hr; 300 ml of 1 *N* HCl was added and the resulting solution was extracted three times with ether. The combined ether extracts were dried over anhydrous magnesium sulfate. After filtration, the ether was removed and the residue was distilled *in vacuo*. The fraction boiling at 145–149° (0.35 mm) weighed 11.4 g (70.4%).

Procedure 2. Reduction of Triethyl α-Phosphonocinnamate in Ethanol.—A solution of 15.6 g (0.05 mol) of triethyl α-phosphonocinnamate in 30 ml of cold, absolute ethanol was added dropwise over 20 min to a mixture of 1.9 g (0.05 mol) of $NaBH_4$ in absolute ethanol at 0–5°. After the addition, the reaction mixture was stirred for 1 hr in the cold and 2 hr at room temperature. Water (400 ml) was then added and the solution was extracted with three 60-ml portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate. After the $MgSO_4$ and ether were removed the product was distilled *in vacuo* at 189–191° (5 mm). The product weighed 11.2 g (70.2%).

Procedure 3. Hydrolysis of Triethyl α-Phosphonocinnamate.—A mixture of 6.3 g (0.02 mol) of triethyl α-phosphonocinnamate and 20 ml of concentrated hydrochloric acid was heated at reflux temperature for 24 hr, allowed to cool to room temperature, and placed in a refrigerator overnight. The dark brown solid was recrystallized from 70% ethanol, producing 1.9 g (64.2%) of product. Two further recrystallizations from dilute ethanol gave white crystals of cinnamic acid, mp 134–135°.

Registry No.—**3** (Ar = Ph), 13507-49-8.