Corey and Chaykovsky,[4,5] derived from 1.0 g (0.041 mole) of NaH and 40 ml of DMSO, was added 4.0 g (0.022 mole) of powdered *trans*-stilbene. The solution immediately turned deep red and heat was evolved. The solution, which was maintained at 25–35° with an ice bath, was stirred for 15 min, and was then added to 200 ml of water. Extraction with 100 ml of CH_2Cl_2, drying, and distillation of the solvent at the water pump left a residue which crystallized in part. The solid, 2.45 g, melted from 77 to 80° (lit.[5] mp 81–82°). The mother liquors chromatographed on neutral alumina and eluted with *n*-hexane, gave an additional 0.29 g of this material: mp 78–80°;[6] yield 67%; infrared $\lambda_{CHCl_3}^{max}$ 6.18, 6.29 μ; nmr (τ_{CCl_4}) 2.42–2.92 (10) multiplet, 3.2 (1) unresolved quartet (J = 2 cps), 7.83 (3) doublet (J = 2 cps) ppm.

General Procedure for the Methylation of Stilbazoles. β-Methyl-2-stilbazole (VII).—To a solution of DMSO anion prepared from 1.0 g (0.041 mole) of NaH and 40 ml of DMSO was added dropwise under N_2, a solution of 4.0 g (0.022 mole) of 2-stilbazole in 20 ml of DMSO. Total time for addition and stirring was 1 hr. The solution, which had turned dark brown, was added to 100 ml of water and extracted with 100 ml of CH_2Cl_2. Drying, followed by distillation of the solvent at the water pump left a residue which upon distillation *in vacuo* gave 3.28 g of material: bp 110–114° (0.4 mm); yield 77%; infrared $\lambda_{CHCl_3}^{max}$ 6.10, 6.28 μ. On a 5-ft column, packed with 20% SE 30 on Chromosorb W, column temperature 200°, flow rate 86 ml/min, this material had a retention time of 6.5 min. With equivalent conditions, VIII had a retention time of 7 min. *Anal.* Calcd for $C_{14}H_{13}N$: C, 86.12; H, 6.71. Found: C, 86.18; H, 6.84.

Also prepared in this manner was **β-methyl-3-methyl-2-stilbazole (XIV)**: yield 67%; bp 100–107° (0.07 mm); infrared $\lambda_{CCl_4}^{max}$ 6.15, 6.33 μ; ultraviolet λ_{EtOH}^{max} 312 mμ (ϵ 11,600), 272 mμ (ϵ 11,200); nmr (τ_{CCl_4}) 1.43 (1) doublet (J = 5 cps), 2.3–4.4 (8) multiplet, 7.46 (3) doublet (J = 1.5 cps), 7.9 (3) singlet ppm. *Anal.* Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.03; H, 7.40; N, 6.52. **β-Methyl-3-methyl-4-stilbazole (XV)** was also prepared by this method: yield 51%; bp 107–108° (0.1 mm); infrared $\lambda_{CHCl_3}^{max}$ 6.18, 6.31 μ; ultraviolet λ_{EtOH}^{max} 268 mμ (ϵ 13,000); nmr (τ_{CCl_4}) 1.50–1.85 (2) multiplet, 2.4–3.4 (7) multiplet, 7.96 (3) singlet, 8.05 (3) doublet (J = 1.5 cps) ppm., *Anal.* Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22. Found: C, 85.74; H, 7.16. **β-Methyl-5-methyl-2-stilbazole (XVI)** was prepared in the same way: yield 37%; bp 126–128° (0.25 mm); mp 40–41°; infrared $\lambda_{CCl_4}^{max}$ 6.14, 6.25 μ; ultraviolet, λ_{EtOH}^{max} 296 mμ (ϵ 15,400), 271 mμ (ϵ 14,800); nmr (τ_{CCl_4}) 1.67 (1) broad singlet, 2.45–3.40 (8) multiplet, 7.48 (3) doublet (J = 1.51 cps), 7.87 (3) singlet ppm. *Anal.* Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22. Found: C, 85.85; H, 7.22.

General Procedure for the Hydrogenation of Stilbazoles. 1-(2-Pyridyl)-2-phenylpropane (X).—Hydrogenation of 3.22 g (0.017 mole) of VII was carried out at room temperature and atmospheric pressure, in 20 ml of absolute ethanol, using 0.5 g of Pd–C. The catalyst was filtered after 410 ml of H_2 had been absorbed (required 380 ml). Distillation of the ethanol at the water pump left a residue, which upon distillation *in vacuo* gave 2.91 g of material: bp 78–80° (0.07 mm); yield 86%; infrared $\lambda_{CCl_4}^{max}$ 6.30, 6.38 μ; nmr (τ_{CCl_4}) 1.72 (1) doublet (J = 5 cps), 2.68–3.42 (8) multiplet, 6.5–7.4 (3) multiplet, 8.8 (3) doublet (J = 8 cps) ppm. *Anal.* Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66. Found: C, 85.37; H, 7.81.

Also prepared in this manner was **1-(3-methyl-2-pyridyl)-2-phenylpropane (XVII)**: yield 90%; infrared $\lambda_{CCl_4}^{max}$ 6.36 μ; ultraviolet λ_{EtOH}^{max} 267 mμ (ϵ = 4700); nmr (τ_{CCl_4}) 1.53 (1) doublet (J = 5 cps), 2.66–3.33 (7) multiplet, 6.2–7.1 (3) multiplet, 8.08 singlet, 8.70 (3) doublet (J = 7 cps) ppm. *Anal.* Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.02; H, 8.29; N, 6.80. **1-(3-Methyl-4-pyridyl)-2-phenylpropane (XIX)** was prepared in this way: yield 70%; infrared, $\lambda_{KHCl_3}^{max}$ 6.29 μ; ultraviolet λ_{EtOH}^{max} 264 mμ (ϵ 5800); nmr (τ_{CCl_4}) 1.6–1.9 (2) multiplet, 2.7–3.4 (6) multiplet, 6.3–7.2 (3), 8.24 (3) singlet, 8.9 (3) doublet (J = cps) ppm. *Anal.* Calcd for $C_{15}H_{16}N$: C, 85.26, H, 8.11. Found: C, 85.40; H, 8.25.

Acknowledgment.—The authors wish to thank the Amerian Cancer Society for their generous support of this work.

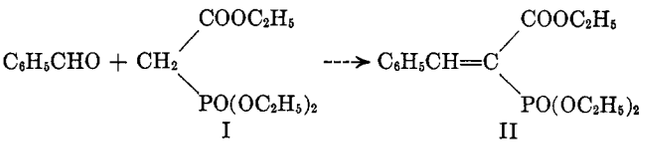
Condensation of Triethyl Phosphonoacetate with Aromatic Aldehydes

CHARLES N. ROBINSON AND JOHN F. ADDISON[1]

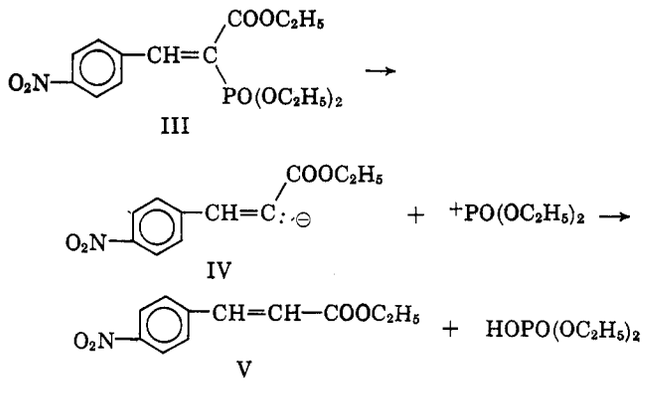
Department of Chemistry, Memphis State University, Memphis, Tennessee 38111

Received May 9, 1966

The condensation of triethyl phosphonoacetate (I) with benzaldehyde on heating at 160–170° with acetic anhydride was reported by Pudovik and Lebedeva[2] to give a 37–40% yield of triethyl benzylidenephosphonoacetate (II).



In a reinvestigation of this work, Patai and Schwartz[3] obtained lower yields (17%) of the ester (II) under the conditions used by the Russian authors but were able to obtain much better yields (70%) of the triester by using milder reaction conditions (refluxing benzene as a solvent, piperidine and acetic acid as catalysts) and longer reaction time. They also found that with *p*-nitrobenzaldehyde and triethyl phosphonoacetate in ethanol as the solvent and piperidine as the catalyst, very high yields (83%) of ethyl *p*-nitrocinnamate (V) were obtained, but that no phosphorus-containing ester (III) could be isolated. They believe that the dephosphonation in this case is due to the increased stabilization by the nitro group of the carbanion (IV) formed in the elimination.



We have prepared a number of the triesters analogous to II with substituents on the aromatic ring which are electron donating or not so strongly electron withdrawing as the nitro group. The conditions used for the condensation reactions were analogous to the conditions used by Patai and Schwartz in which they obtained their best yield. Refluxing benzene was used as the solvent with a Dean–Stark trap so that the progress of the reaction could be followed as water

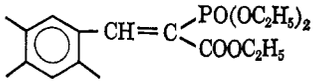
(1) (a) The authors gratefully acknowledge the support of this work by the National Institutes of Health, U. S. Public Health Service (GM-12480-01); (b) part of the work discussed in this article is abstracted from work presented for the M.S. thesis by J. F. Addison.

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

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

TABLE I

TRIETHYL ARYLIDENEPHOSPHONOACETATES



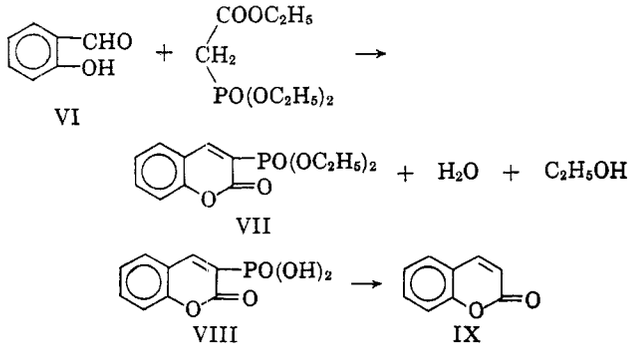
No.	Starting aldehyde	Reflux period, days	Bp of triester, °C (mm)	Yield, %	Formula	Anal, % Calcd C	Calcd H	Calcd P	Found C	Found H	Found P
1	Benzaldehyde	3	154–158 (0.35)	63.0	$C_{15}H_{21}O_5P$						
2	*p*-Chlorobenzaldehyde	6	182 (0.40)	25.5	$C_{15}H_{20}O_5PCl$	51.94	5.77	8.94	51.77	5.88	8.71
3	*p*-Tolualdehyde	5	162 (0.15)	36.0	$C_{16}H_{23}O_5P$	58.90	7.06	9.51	59.05	7.92	9.48
4	Anisaldehyde	6	184–186 (0.30)	69.0	$C_{16}H_{23}O_6P$	56.14	6.73	9.06	55.82	6.95	9.00
5	Veratraldehyde	5	210 (0.70)	36.0	$C_{17}H_{25}O_7P$	54.83	6.77	8.32	54.91	6.50	7.95
6	1-Naphthaldehyde	7	197 (0.30)	28.3	$C_{19}H_{23}O_5P$	62.98	6.35	8.56	62.59	6.66	8.61
7	Salicylaldehyde[a]	1.5	...	61.4							

[a] The ester was not isolated in this case; the yield is based on the hydrolysis product, coumarin-3-phosphonic acid.

was formed and removed by azeotropic distillation. Piperidine and benzoic acid were used as catalysts.

Although the yields varied widely, no problems were encountered in preparing the esters indicated in Table I except in their purification. All the compounds are high-boiling liquids and some of them had to be distilled two or three times before they were pure enough for analysis; the reported yields are based on the purified products.

Attempts were also made to condense the ketones, acetophenone, benzophenone, and 9-fluorenone, but these compounds apparently did not react as no water was formed and no products other than starting materials could be isolated. Salicylaldehyde (VI), however, reacts smoothly with triethyl phosphonoacetate, although the product of this reaction could not be purified owing to its high boiling point. We assume that this compound is the diethyl ester of coumarin-3-phosphonic acid (VII) for several reasons. The reaction between salicylaldehyde and diethyl malonate is known to produce 3-carbethoxycoumarin,[4] and the volume of the aqueous phase collected in the Dean–Stark trap during our condensation was greater than the theoretical amount of water. This phase gave a positive iodoform test and was shown by vpc analysis to be approximately 50% ethanol. Finally, when this crude material was hydrolyzed with hot, concentrated hydrochloric acid, a dark brown solid formed which was readily purified and which proved to be coumarin-3-phosphonic acid (VIII). This compound is a high-melting, stable solid which undergoes dephosphonation to coumarin (IX) only at high temperatures.



The infrared spectra of the purified esters (liquid smear of neat compound) in Table I are consistent with the structures assigned. All of them have absorption bands at 1230–1260 cm^{-1} (s) (P=O stretching vibration[5]), 1150–1170 cm^{-1} (w) (PO-ethyl), 990–1050 (vs) (PO-alkyl), and near 980 (s) (POC). There are also strong sharp peaks near 1750 (C=O stretching) and 1220 (CO stretching).

(4) N. D. Cheronis, "Semimicro Experimental Organic Chemistry," The Hadrian Press, New York, N. Y., 1960, p 317.

Experimental Section

The benzene, piperidine, benzoic acid, and all of the aldehydes used as starting materials were commercial products. Triethyl phosphonoacetate was prepared by the method of Wiley[6] in 76% yield. All melting points were obtained on a Fischer-Johns melting point apparatus. Analyses were by Schwartzkopf Microanalytical Laboratories, Woodside, N. Y.

All of the esters listed in Table I were prepared by essentially the same procedure and are illustrated by the following.

Preparation of Triethyl 4-Methoxybenzylidenephosphonoacetate.—A mixture of 7.0 g (0.05 mole) of anisaldehyde and 12.0 g (0.05 mole) of triethyl phosphonoacetate in 100 ml of benzene was placed in a 300-ml flask equipped with a Dean–Stark trap and a reflux condenser. Piperidine (0.5 ml) and benzoic acid (0.5 g) were added and the solution was refluxed for 6 days (until the volume of water in the trap remained unchanged for 24 hr). The benzene was removed by distillation and the residue was distilled *in vacuo*. The fraction boiling at 180–220° (2.4 mm) was collected. This bright yellow fraction was redistilled to give 12.5 g (69%) of the ester boiling at 184–186° (0.3 mm).

Preparation of Coumarin-3-phosphonic Acid.—To a 300-ml flask equipped with a Dean–Stark trap and reflux condenser were added 28.5 g (0.116 mole) of triethyl phosphonoacetate, 12.5 g (0.103 mole) of salicylaldehyde, 100 ml of benzene, 0.5 g of benzoic acid, and 0.5 ml of piperidine. The reaction mixture was allowed to reflux for 36 hr (the volume of the aqueous phase in the trap was 3.15 ml), then the benzene was removed by distillation. To the crude yellow residue, which is presumably the diethyl ester of coumarin-3-phosphonic acid, was added 60 ml of concentrated hydrochloric acid and refluxing was continued for 24 hr. The reaction mixture was cooled to room temperature and the solid which had formed was removed by filtration, dissolved in ethanol, decolorized with Darco, and recrystallized by adding an equal volume of water to give 20.5 g of light brown crystals. After twice more being recrystallized from absolute ethanol 14.3 g (61.4%) of white needles was obtained which melted sharply at 256–257°. An analytical sample recrystallized twice from water and finally from absolute ethanol and dried over P_2O_5 at 65° melted at 268–269°.

Anal. Calcd for $C_9H_7O_5P$: C, 47.80; H, 3.12; P, 13.70. Found: C, 47.52; H, 3.40; P, 13.60.

Thermal Decomposition of Coumarin-3-phosphonic Acid.—Five grams (0.022 mole) of the acid was placed in a distilling flask and heated *in vacuo* at a bath temperature of 270–300°. A pale yellow oil (1.84 g, 57%) which quickly solidified was collected. After recrystallization from ethanol this solid melted at 68–69° and admixed with coumarin at 69–70°.

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1960.

(6) R. H. Wiley, U. S. Patent 2,478,441 (1949); *Chem. Abstr.*, **44**, 2010*b* (1950).