

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

Addition Reactions in Phospho-organic Syntheses. I. The Addition of Phosphorus Pentachloride to Olefins

BY GENNADY M. KOSOLAPOFF AND W. FREDERICK HUBER

The synthesis of α,β -unsaturated phosphonic acids by the addition of phosphorus pentachloride to unsymmetrical olefins was discovered by J. Thiele,¹ who failed, however, to give the customary experimental data in his brief communication.

Two decades later, this reaction was explored in considerable detail by Bergmann and Bondi,² particularly in the field of unsymmetric diaryl olefins.

The phosphorus pentachloride addition offers an elegant method of preparation of a variety of phospho-organic derivatives from hydrocarbons. For this reason it was felt desirable to investigate its possibilities in the syntheses of phosphonic acids from substituted styrenes. Information as to the limitations imposed by steric hindrance effects was also felt to be of interest.

Accordingly, a number of substituted styrenes were treated with phosphorus pentachloride, in benzene suspension, to give, after hydrolysis, the

2-Phenylstyrene- β -phosphonic acid, which was prepared in the course of this investigation, offered an interesting possibility of conversion to the 9-phenanthrylphosphonic acid. However, dehydrogenation of the former compound with sulfur gave a product which apparently was not the phenanthrene derivative; the nature of the product was left open because of the extremely poor yields.

Since the addition of phosphorus pentachloride to reactive olefins proceeds with considerable rapidity, it was felt that the reaction might be carried out by means of "nascent" phosphorus pentachloride, *i.e.*, by the passage of chlorine into a solution of the olefin in phosphorus trichloride. This possibility was confirmed in the case of styrene in that substantial yields of β -styrenephosphonic acid and styrene dichloride were obtained, thus showing that the addition of phosphorus pentachloride and of chlorine to the vinyl group proceed at comparable rates.

TABLE I

$\text{RCH}=\text{CHPO}_3\text{H}_2$ R =	M. p., °C.	Anal., Found	% P Calcd.	Olefin used, g.	PCl ₅ , g.	Yield, g.	Crystallization solvent
2,4-Dimethylphenyl	142-143	14.32 13.99	14.6	13.2	25	9.9	Water
2,4,6-Trimethylphenyl	176-178	13.64 13.61	13.7	10.0	16.6	8.0	Dilute alcohol
4-Ethylphenyl	138-140	14.63	14.59	32.0	50.0	20.0	Ethylbenzene
2- <i>t</i> -Butylphenyl	188-189	Eq. wt. 122.1	Eq. wt. 120	1.0	2.0	0.5	Hot water
4- <i>t</i> -Butylphenyl	150.5-151.5	13.05 12.87	12.9	10.0	15.0	7.0	Dilute alcohol
2-Biphenyl	186-188	Eq. wt. 132	Eq. wt. 130	2.8	5.0	2.3	Water
3-Biphenyl	156-157.5	11.79 11.66	11.91	6.5	10.4	5.0	Pptn. by HCl from NaOH soln.
4-Biphenyl	193-193.5	11.81 11.62	11.91	39.8	52.0	22.8	Butanol
2-Naphthyl	181.5-182	12.93 13.16	13.17	50.0	67.4	32.0	Acetic acid
2-Fluorenyl	200-205 dec.	11.53 11.56	11.4	16.3	17.7	8.0	EtOH-PrOH
2,4,4-Trimethyl-1-pentene- phosphonic acid	104-105	16.10	16.15	Commercial di- isobutylene, 56.0	104.0	30.0	Ether-hexane

desired phosphonic acids in satisfactory yields. It was found that the substitution of a methyl, a phenyl or a *t*-butyl group in the position ortho to the vinyl group failed to prevent the addition of phosphorus pentachloride to the latter.

(1) J. Thiele, *Chem. Ztg.*, **36**, 657 (1912).(2) E. Bergmann and A. Bondi, *Ber.*, **63**, 1158 (1930); **64**, 1455 (1931); **66**, 278 (1933).

The preparation of 4-phenyl-1,3-butadiene-1-phosphonic acid was reported by Bergmann and Bondi in a 55% yield. We found that the use of an effective stirrer (Hershberg wire stirrer) resulted in an 88.7% yield of this acid, as compared with the lower yield secured with the use of the conventional glass stirrer. However, no appreciable yield improvements were noted in this con-

nection in the case of other vinyl compounds.

One new aliphatic phosphonic acid, 2,4,4-trimethyl-1-pentenephosphonic acid, was prepared from commercial di-isobutylene.

Experimental

The procedure used was essentially that of Bergmann and Bondi. The experimental data and the constants of the new compounds are given in the preceding table.

Attempted Ring Closure of 2-Phenylstyrene- β -phosphonic Acid.—2-Phenylstyrene- β -phosphonic acid (1.0 g.) was heated for twenty-five minutes with 0.2 g. of sulfur at 230–240°. The brisk evolution of hydrogen sulfide was essentially complete in twenty minutes. The cooled mass was extracted with dilute sodium hydroxide and the alkaline extract was added slowly to warm dilute hydrochloric acid to give 0.2 g. of the dehydrogenation product, which formed tiny colorless flakes and decomposed at 160–162°. Pyrolysis of this material yielded a small amount of yellowish liquid which could not be induced to crystallize and which failed to exhibit the typical fluorescence of phenanthrene in ultraviolet light. Although the product does not appear to be the desired phenanthrene derivative, further investigation of its nature was prevented by the meager yields.

Reaction of Styrene, Phosphorus Trichloride and Chlorine.—A solution of 52.1 g. (0.5 mole) of styrene in 500 cc. of dry benzene was treated with 68.7 g. (0.5 mole) of phosphorus trichloride. Dry chlorine was introduced into the solution with vigorous stirring and cooling by

means of an ice-bath. After five hours, the mixture assumed a yellowish color due to the presence of free chlorine. At this point the mixture was in the form of a creamy suspension of the styrene-phosphorus pentachloride adduct. The mixture was hydrolyzed with 200 grams of ice, after which the spontaneous evaporation of the benzene layer gave 32.9 g. (35.7%) of β -styrene-phosphonic acid, m. p. 140–144°. The filtrate deposited 43.4 g. (49.6%) of styrene dichloride, as a heavy oil, b. p. 105–120° at 10.5 mm., n_D^{25} 1.5553.

β -Styrenephosphonic acid was readily purified by slow addition of its solution in dilute sodium hydroxide to warm dilute hydrochloric acid with stirring. Recrystallization from hot water gave the product in the form of lustrous colorless plates, m. p. 154.5–155°. The addition of hydrochloric acid to a solution of the styrenephosphonic acid in dilute sodium hydroxide, however, yields a poorly soluble acid sodium salt which forms colorless plates which melt indefinitely at 224–227°.

Summary

Ten new unsaturated phosphonic acids were prepared by the addition of phosphorus pentachloride to the corresponding olefins.

The addition of phosphorus pentachloride and of chlorine to styrene was shown to be competitive.

DAYTON, OHIO

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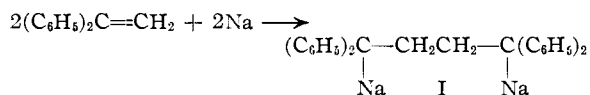
(3) Original manuscript received April 3, 1946.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

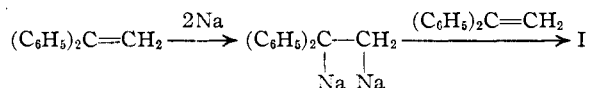
The Reduction of Unsaturated Hydrocarbons at the Dropping Mercury Electrode. III. Mechanism of the Dimerizing Addition of Sodium to Olefins^{1,2}

BY STANLEY WAWZONEK AND JOYCE WANG FAN³

Certain types of olefins when treated with alkali metals add and dimerize in a similar manner to that shown for 1,1-diphenylethylene.



Two mechanisms have been proposed for the formation of the dimer (I). Ziegler and co-workers⁴ have suggested that the reaction follows normal 1,2-addition with the resulting organo-alkali compound adding to another molecule of



olefin. Schlenk and Bergmann⁵ have proposed free radical formation as the initial step followed by polymerization.

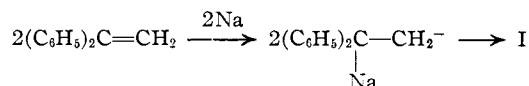
(1) Paper II, Wawzonek and Laitinen, *THIS JOURNAL*, **64**, 2365 (1942).

(2) Presented before the Division of Organic Chemistry of the American Chemical Society at the Chicago meeting, September, 1946.

(3) Abstracted from a thesis by Joyce Wang Fan, presented to the Graduate College of the State University of Iowa, in partial fulfillment of the requirements for the Ph.D. degree, June, 1946.

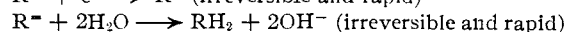
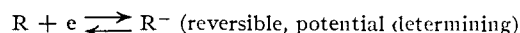
(4) Ziegler, Colonius and Schafer, *Ann.*, **473**, 36 (1929).

(5) Schlenk and Bergmann, *ibid.*, **463**, 1 (1928).



Chemical evidence offered up to the present time has not been able to distinguish between these mechanisms.⁶

The behavior of unsaturated hydrocarbons at the dropping mercury electrode has been found in previous work¹ to resemble that observed with alkali metals. Both are sources of electrons with the dropping mercury electrode having the advantage of being a controlled source. Therefore the mechanisms of reduction at each should be comparable. Work⁷ with 1,1-diphenylethylene has indicated the following mechanism for its electroreduction.



This mechanism is in essential agreement with Ziegler's hypothesis. The second electron adds before the free radical can dimerize. The resulting products at the dropping mercury electrode differ from those obtained with sodium in this respect.

(6) Wooster, *Chem. Rev.*, **11**, 1 (1932).

(7) Laitinen and Wawzonek, *THIS JOURNAL*, **64**, 1765 (1942).