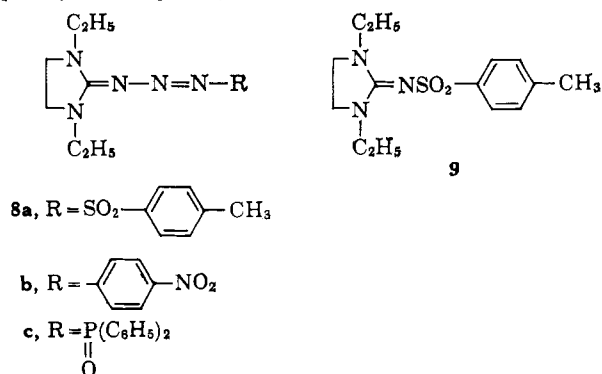
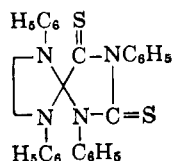


taining one less molecule of nitrogen.⁶ Dropwise addition of **1a** to a benzene solution of *p*-toluenesulfonyl azide at 0° gives 31% of **8a** as bright yellow crystals, m.p. 109–110° dec. The imino derivative **9** can be isolated from the mother liquors as a white solid, m.p. 94–96°. Under similar reaction conditions **1a** and *p*-nitrophenyl azide give 35% of **8b** as orange crystals, m.p. 108–108.5° dec., while diphenylphosphonyl azide gives yellow **8c**, m.p. 145.5–146.5° dec.



papers. These compounds are much less reactive than the alkyl-substituted bis(imidazolidines) of this report. However, under more rigorous reaction conditions **1** (R = C₆H₅) reacts with phenyl isothiocyanate giving the dithio derivative



m.p. 206–208°. With refluxing phenyl isocyanate, **1** (R = C₆H₅) gives the corresponding spirohydantoin, m.p. 253–255°, in 79% yield. The more basic alkyl-substituted bis(imidazolidines) cause trimerization of phenyl isocyanate to triphenyl isocyanurate.

(6) See R. W. Hoffmann and H. Häuser, *Tetrahedron Letters*, 1365 (1964), and H. Quast and S. Hünig, *Angew. Chem.*, **76**, 989 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 800 (1964), for cleavage reactions of other positively-substituted ethylenes with azides.

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Acetylenes and α -Chlorostilbenes via Phosphonate Anion

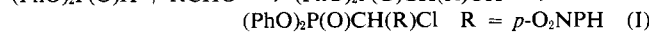
Sir:

The Wittig reaction has been used extensively to synthesize olefins.¹ Reactions of this type which lead to chloro-substituted olefins are much less numerous.^{2–5} The synthesis of an acetylene according to this method has been described only recently.^{6,7} An arylcarbalkoxymethylenetriphenylphosphorane is heated to about 250° and undergoes decomposition into triphenylphosphine oxide and acetylene. The latter author mentioned that this synthesis proceeds poorly, if at all, by the

Horner–Emmons^{8,9} variation of this synthesis, using phosphonate carbanions.

We wish to report in this communication first results of a synthetic method for chlorostilbenes and acetylenes, utilizing appropriately substituted phosphonates, which proceeds under very mild conditions, thus permitting sensitive functional groups to be part of the acetylenes or chlorostilbenes to be synthesized.

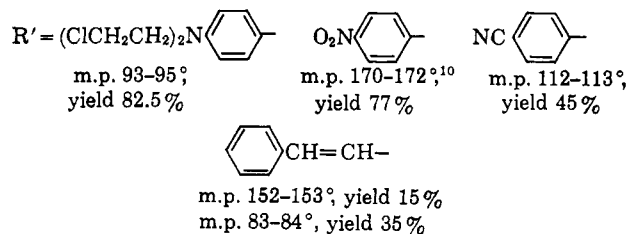
Diphenyl phosphite is condensed with an aromatic aldehyde to yield diphenyl 1-hydroxy-1-arylmethane-phosphonate. These compounds are converted by POCl₃ treatment into the corresponding chloro compounds, diphenyl 1-chloro-1-arylmethane-phosphonate (**I**). **I**, upon treatment with 1 equiv. of NaH in THF



(or much better DMSO) (eq. a) yields a deeply colored anion which reacts with aldehydes to yield α -chlorostilbenes; if at least 2 equiv. of base is used (eq. b) one obtains acetylenes.

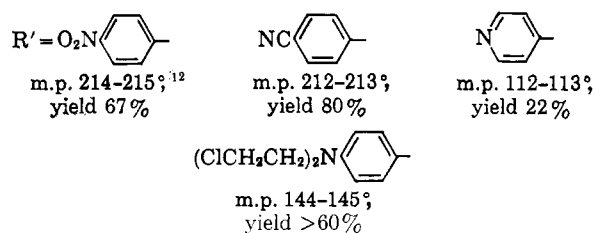


The following α -chlorostilbenes were prepared.



For the preparation of 1-chloro-1-(4-nitrophenyl)-4-phenylbutadiene *trans*-cinnamaldehyde was used; according to the ultraviolet data of the two isolated isomers the higher melting form is tentatively assigned the *trans,trans* configuration [λ 369 m μ (ϵ 27.7 \times 10³)] (with respect to phenyl groups) and the lower melting one is believed to be the *trans,cis* isomer [λ 362 m μ (ϵ 15.6 \times 10³)] (also with respect to phenyl groups). Both isomers after irradiating for several hours gave ultraviolet absorption curves which were nearly identical, indicating that photoequilibrium was reached.

The following acetylenes were obtained by eq. b; they were characterized by their C, H, and N analyses¹¹ and infrared spectra.



(8) L. Horner, H. Hoffmann, and H. G. Wippel, *Ber.*, **91**, 61 (1958).

(9) W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

(10) P. Pfeiffer and E. Kramer, *Ber.*, **46**, 3655 (1913), m.p. 144°; the stereochemistry of the reported nor derivative of the present product is known.

(11) All analyses of the compounds reported in this communication were in agreement with the calculated values within 0.4%. The yields undoubtedly can be improved; the reported ones are in most cases based on one run only.

(12) M.p. 211–212° (ref. 10).

(1) G. Wittig, *Pure Appl. Chem.*, **9**, 245 (1964).

(2) D. Seyferth, S. O. Grim, and T. O. Read, *J. Am. Chem. Soc.*, **82**, 1510 (1960); **83**, 1617 (1961); D. Seyferth, J. K. Heeren, and S. O. Grim, *J. Org. Chem.*, **26**, 4783 (1961).

(3) A. J. Speziale, G. J. Marco, and K. W. Ratts, *J. Am. Chem. Soc.*, **82**, 1260 (1960).

(4) G. Wittig and M. Schlosser, *Ber.*, **94**, 1373 (1961).

(5) G. Märkl, *ibid.*, **94**, 2996 (1961).

(6) G. Märkl, *ibid.*, **94**, 3005 (1961).

(7) S. T. D. Gough and S. Trippett, *Proc. Chem. Soc.*, 302 (1961); *J. Chem. Soc.*, 2333 (1962); S. Trippett, *ibid.*, 2335 (1962).

Typical procedure for obtaining an α -chlorostilbene is as follows: In 10 ml. of THF 2.02 g. (0.005 mole) of I is dissolved and cooled below 0°. This solution is treated at once with 1 equiv. of 10% methanolic KOH, whereupon a deep purple color develops. This colored solution is treated with 0.005 mole of the *p*-bis(2-chloroethyl)aminobenzaldehyde in 5 ml. of THF. The deep purple color slowly disappears. After standing for about 24 hr. a yellow precipitate forms. The solvent is evaporated under vacuum and the residue is treated with distilled water and filtered. After recrystallizations from 95% ethanol it melted at 93–95°.

Typical procedure for obtaining an acetylene is as follows: In a 125-ml. erlenmeyer flask 2.02 g. (0.005 mole) of I and 0.7 g. (0.005 mole) of *p*-cyanobenzaldehyde were placed and dissolved in 25 ml. of dry DMSO.

To this solution was added 1 equiv. of NaH. After the initial reaction had subsided a second equivalent of NaH was added. After all bubbling had ceased the deep red mixture was diluted with water and extracted twice with 50-ml. portions of ether. The ether extracts were combined, dried, and evaporated under vacuum. The residue was dissolved in methanol, filtered, and recrystallized twice from methanol–water; it yielded 1.0 g. (80%) of the acetylene, m.p. 212–213°.

The scope and limitation of this reaction is actively being investigated by us.

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Book Reviews

Electronic Aspects of Biochemistry. Proceedings of the International Symposium Held at Ravello, Italy, September 16–18, 1963, Sponsored by NATO. Edited by BERNARD PULLMAN, Université de Paris, Institut de Biologie Physico-Chimique, Paris, France. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1964. xii + 582 pp. 16 × 24 cm. \$20.00.

Owing, in very large part, to the research, writings, and interest of Professors Bernard and Alberté Pullman, the subject of quantum mechanics is now being discussed on a level that can be understood and utilized by biochemists. For the past two summers an International Summer Institute has been organized by Professor B. Pullman to bring together chemists, biologists, and physicists who have in common the desire to apply quantum mechanics to biological problems. The book under review contains 33 papers presented at a Symposium at the end of the first such summer school, at Ravello, Italy, in 1963.

It is not only impossible to give an adequate review to a book containing papers on 33 different subjects, but it seems pointless to even list the 33 subjects discussed. Suffice it to say that lucid papers of interest to biologists are presented on the use of fluorescence, optical rotation, Mössbauer effect, and electrical conductance. Quantum mechanical concepts and interpretations are introduced into biological energy transfer, carcinogenesis, intermolecular forces, replication and mutation, radiation effects, and biochemical reactions of various types.

Although every aspect of this book should be of great interest to all biochemists, the average biochemist with no knowledge of quantum mechanics will find most of it incomprehensible. However, most of the book can be understood by those having only an elementary knowledge of quantum mechanics. Several papers require even more advanced training.

This reviewer does not urge all biochemists and biophysical chemists to purchase the book—only those who are interested in keeping in the forefront of the fascinating new field of quantum biochemistry, or quantum biophysics, and who will take the trouble to learn the necessary tool of elementary quantum mechanics.

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Proceedings of the 1962 Tihany Symposium. Radiation Chemistry.

Edited by JANOŠ DOBÓ, Research Institute for the Plastics Industry, Budapest, and G. V. PUTIRSKAYA, Central Chemical Research Institute of the Hungarian Academy of Sciences. Akademiai Kiado, Publishing House of the Hungarian Academy of Sciences, Budapest V, Hungary. 1964. 482 pp. 16 × 22.5 cm. \$14.00.

This book contains 50 research papers presented at the Tihany Symposium in Radiation Chemistry in Hungary in September 1962. The book is divided into sections on the radiation chemistry of (1) organic compounds, (2) polymeric systems, (3) aqueous solutions, and (4) dosimetry and miscellaneous subjects. Sixteen papers originate from the German Federal Republic (West Germany), France, or the United Kingdom. The remainder are from the USSR, Hungary, Poland, German Democratic Republic (East Germany), Czechoslovakia, or Roumania. All of the papers are in English, in fact, in excellent English.

Many of the reports are variations of papers that have been or will be published in the regular scientific journals. The papers are usually short, 6–7 pages, do not give any experimental details, and often have very brief or superficial discussions. Exceptions to this are two long reports on electron spin resonance studies by Voevodski (USSR) and Sharpaty (USSR).

This book is of some value to the specialist in radiation chemistry, for it provides a convenient introductory compilation to the radiation chemistry work of East European countries and gives references to important publications in the Russian literature. However, the book is of doubtful value to most libraries. The papers were already 2 years old when published and are now 3 years old. Many of the papers are fragmentary and the important work is covered mostly in regular scientific journals.

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