

a direct investigation of this hypothesis is now possible. The results of such studies will be reported shortly.

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(b) A. W. Fort, *J. Am. Chem. Soc.*, **84**, 2620 (1962); (c) *ibid.*, **84**, 2625, 4979 (1962); (d) R. C. Cookson and M. J. Nye, *J. Chem. Soc.*, 2009 (1965); (e) R. Loftfield, *J. Am. Chem. Soc.*, **72**, 632 (1950); (f) *ibid.*, **73**, 470 (1951); J. G. Burr, Jr., and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954).

(17) National Science Foundation Predoctoral Fellow 1964-1965.

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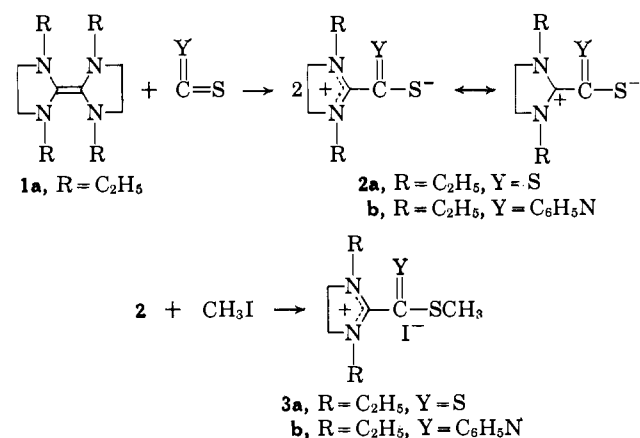
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## Chemistry of Peraminoethylenes

Sir:

Aliphatic peraminoethylenes, particularly the  $\Delta^{2,2'}$ -bis(imidazolidines) (**1**), are extremely reactive, powerful  $\pi$ -bases.<sup>1</sup> They are readily converted by carbon disulfide to orange- to red-colored stable dithioquaternary salts (**2**, Y = S) or by aryl isothiocyanates to stable yellow-colored mercapto-N-arylformimidoyl-imidazolium inner salts (**2**, Y = ArN) in high yield.<sup>2</sup> The inner salts **2** undergo rapid alkylation by methyl iodide forming the water-soluble iodides (**3**). For



example, 1,1',3,3'-tetraethyl- $\Delta^{2,2'}$ -bis(imidazolidine) (**1a**) reacts exothermally with carbon disulfide, precipitating **2a** (dark red, m.p. 178-179°, 98% yield), which is converted quantitatively by methyl iodide to **3a** (dark red, m.p. 164-166°).<sup>3</sup> The exothermic reaction of **1a** in tetrahydrofuran with phenyl isothiocyanate gives **2b** (light yellow, m.p. 145-147°, 91% yield). Methyl iodide quantitatively converts **2b** to **3b** (colorless, m.p. 184-186°). S-Methylation rather than N-methylation occurs as indicated by spectral

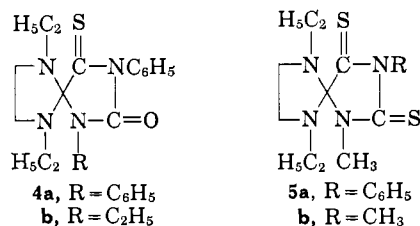
(1) H. E. Winberg, J. E. Carnahan, D. D. Coffman, and M. Brown, *J. Am. Chem. Soc.*, **87**, 2055 (1965).

(2) The inner salts are formally analogous to the adducts of tertiary phosphines with carbon disulfide and phenyl isocyanate; see (a) L. Horner and H. Hoffmann in "Newer Methods of Preparative Organic Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1963, p. 164; (b) T. N. Margulis and D. H. Templeton, *J. Am. Chem. Soc.*, **83**, 995 (1961).

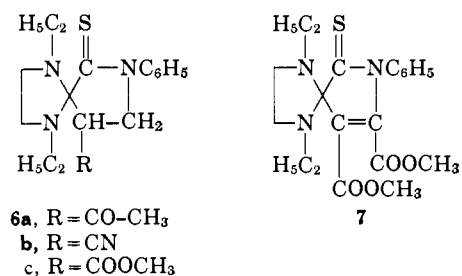
(3) Satisfactory elemental and spectral analyses were obtained for all compounds. All reactions involving the peraminoethylenes were carried out under nitrogen.

analysis of the iodides and isolation of aniline after acid hydrolysis of **3b**.

The inner salts (**2** (Y = ArN)) derived from aryl isothiocyanates represent a new 1,3-dipolar system<sup>4</sup> which undergoes cycloaddition with suitable dipolarophiles, including aliphatic and aromatic isocyanates, aliphatic isothiocyanates, and multiple carbon-carbon bonds. Thus, reaction of **2b** with isocyanates under mild conditions forms the spiroheterocyclics **4**. For example, addition of phenyl isocyanate to **2b** suspended in tetrahydrofuran causes a mild exothermic reaction with the formation of **4a** as a bright yellow solid, m.p. 142-144°. Hydrolysis of **4a** gives 1,3-diphenylurea, confirming the assigned structure. Ethyl isocyanate and **2b** give **4b** (bright yellow, m.p. 104-106°, 75% yield). In a similar manner cycloaddition of methyl isothiocyanate to **2b** gives the dithiohydantoin derivative **5a** (bright yellow, m.p. 129.5-131°, high yield).



Unsaturated compounds such as methyl vinyl ketone, methyl acrylate, and acrylonitrile readily cycloadd to **2b** forming compounds **6**. The reaction, carried out in refluxing tetrahydrofuran, gives the following light yellow-colored adducts: **6a**, m.p. 123.5-124.5°, 76%; **6b**, m.p. 115-117°, 79%; and **6c**, m.p. 123-124° dec., 73%. Under the same conditions, dimethyl acetylenedicarboxylate forms 79% of the unsaturated spiroheterocyclic **7**, m.p. 137-138.5°.



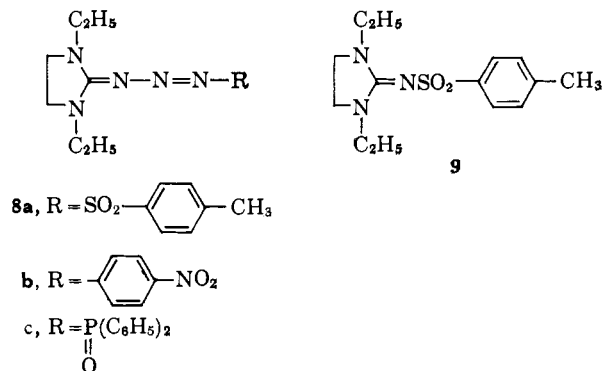
Although under mild conditions the reaction of aliphatic peraminoethylenes with aromatic isothiocyanates proceeds only to the inner salts **2b**, the more reactive aliphatic isothiocyanates give dithiospiroheterocyclics directly, presumably by 1,3-addition of the aliphatic isothiocyanate to unisolated inner salts **2** (Y = RN). Reaction of **1a** with methyl isothiocyanate in refluxing ether gives 74% of bright yellow **5b**, m.p. 86-88°.<sup>5</sup>

The aliphatic bicyclic peraminoethylenes react readily with azides to give diazoiminoimidazolidines (**8**) along with the corresponding iminoimidazolidines con-

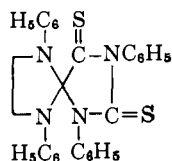
(4) See R. Huisgen [*Proc. Chem. Soc.*, 357 (1961); *Angew. Chem.*, **75**, 604 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963)] for a discussion of 1,3-dipolar cycloadditions. J. E. Baldwin, G. V. Kaiser, and J. A. Romersberger [*J. Am. Chem. Soc.*, **86**, 4509 (1964)] suggest that 1,3-dipolar cycloadditions may be less mechanistically homogeneous than has been previously supposed.

(5) H. W. Wanzlick and his co-workers have extensively studied the chemistry of aryl-substituted bis(imidazolidines) (1, R = aryl); see H. W. Wanzlick and H. Ahrens, *Chem. Ber.*, **97**, 2447 (1964); H. W. Wanzlick and F. Esser, *Angew. Chem.*, **76**, 614 (1964), and earlier

taining one less molecule of nitrogen.<sup>6</sup> 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 ( $R = C_6H_5$ ) reacts with phenyl isothiocyanate giving the dithio derivative



m.p. 206–208°. With refluxing phenyl isocyanate, **1** ( $R = C_6H_5$ ) gives the corresponding spirohydanoin, 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 $\alpha$ -Chlorostilbenes via Phosphonate Anion

Sir:

The Wittig reaction has been used extensively to synthesize olefins.<sup>1</sup> Reactions of this type which lead to chloro-substituted olefins are much less numerous.<sup>2–5</sup> The synthesis of an acetylene according to this method has been described only recently.<sup>6,7</sup> 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

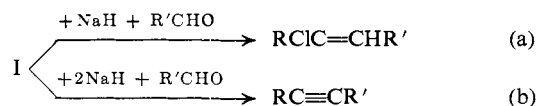
- (1) G. Wittig, *Pure Appl. Chem.*, 9, 245 (1964).
- (2) D. Seyferth, S. O. Grim, and T. O. Read, *J. Am. Chem. Soc.*, 82, 1510 (1960); 83, 1617 (1961); D. Seyferth, J. K. Heeren, and S. O. Grim, *J. Org. Chem.*, 26, 4783 (1961).
- (3) A. J. Speziale, G. J. Marco, and K. W. Ratts, *J. Am. Chem. Soc.*, 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).

Horner–Emmons<sup>8,9</sup> variation of this synthesis, using phosphonate carbanions.

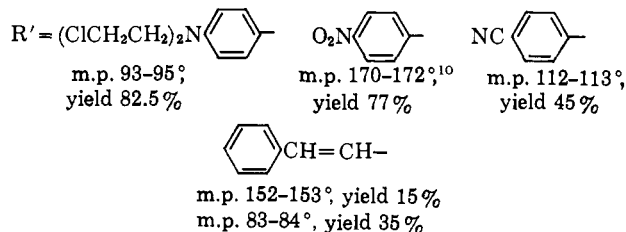
We wish to report in this communication first results of a synthetic method for chlorostilbenes and acetylenes, utilizing appropriately substituted phosphonates, which proceeds under very mild conditions, thus permitting sensitive functional groups to be part of the acetylenes or chlorostilbenes to be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

Diphenyl phosphite is condensed with an aromatic aldehyde to yield diphenyl 1-hydroxy-1-arylmethane-phosphonate. These compounds are converted by POCl<sub>3</sub> treatment into the corresponding chloro compounds, diphenyl 1-chloro-1-arylmethane-phosphonate (I). I, upon treatment with 1 equiv. of NaH in THF

(PhO)<sub>2</sub>P(O)H + RCHO  $\rightarrow$  (PhO)<sub>2</sub>P(O)CH(R)OH  $\rightarrow$  (PhO)<sub>2</sub>P(O)CH(R)Cl R = *p*-O<sub>2</sub>NPh (I)  
 (or much better DMSO) (eq. a) yields a deeply colored anion which reacts with aldehydes to yield  $\alpha$ -chlorostilbenes; if at least 2 equiv. of base is used (eq. b) one obtains acetylenes.

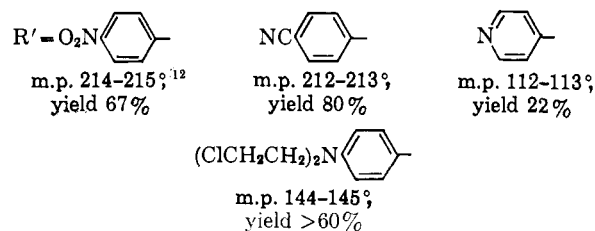


The following  $\alpha$ -chlorostilbenes were prepared.



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 [ $\lambda$  369 m $\mu$  ( $\epsilon$  27.7  $\times$  10<sup>3</sup>)] (with respect to phenyl groups) and the lower melting one is believed to be the *trans,cis* isomer [ $\lambda$  362 m $\mu$  ( $\epsilon$  15.6  $\times$  10<sup>3</sup>)] (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 analyses<sup>11</sup> 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).