

We have also studied the iodination of several nucleoside derivatives with "diiodotriphenylphosphorane" prepared *in situ* by the reaction of triphenylphosphine and iodine.<sup>11</sup> While this reagent appears to be somewhat less reactive than I it was, however, used successfully for the preparation of IIb in 59% yield and of IVe in 50% yield.

Details of these and other studies on the iodination of nucleosides will be presented at a later date.

(11) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964).

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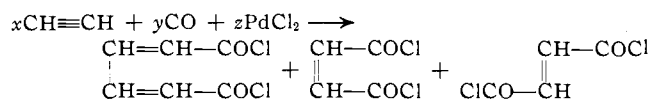
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### Organic Syntheses By Means of Noble Metal Compounds. VI. Synthesis of Muconic Acid<sup>1</sup>

Sir:

We wish to report another new carbonylation<sup>2</sup> reaction of acetylene, namely, the formation of muconyl chloride by a reaction carried out in benzene in the presence of palladium chloride or its complex.<sup>3</sup> The formation of muconic acid from acetylene has been reported before,<sup>4</sup> but only in trace amounts.

In our reaction, muconyl chloride was a major product, accompanied by a considerable amount of fumaryl and maleyl chloride.



In one of the typical examples, a benzene solution of dibenzonitrile-dichloropalladium was placed in a pressure reactor and an acetylene-carbon monoxide mixture

(1) Part V: J. Tsuji, J. Kiji, and S. Hosaka, *Tetrahedron Letters*, No. 12, 605 (1964).

(2) For recent review, see: C. W. Bird, *Chem. Rev.*, **62**, 283 (1962).

(3) Carbonylation of acetylene by the catalytic action of iodide and palladium compounds carried out in alcohol forming esters of acrylic, propionic, maleic, fumaric, and succinic acids was reported: G. Jacobsen and H. Spathe, German Patent 1,138,760 (1962); *Chem. Abstr.*, **58**, 6699 (1963).

(4) P. Pino, A. Miglierina, and E. Pietra, *Gazz. Chim. Ital.*, **84**, 443 (1954).

(1:1) was introduced. The mixture was stirred at room temperature for several hours, and then carbon monoxide was charged up to a pressure of 100 kg./cm.<sup>2</sup>. The mixture was heated to 100°. After the reaction, the formation of acid chloride was confirmed by observing an infrared absorption band at 1800 cm.<sup>-1</sup>. The reaction mixture was refluxed with methanol in order to convert the acid chlorides to the corresponding esters. When the solvent was removed, the residue solidified on standing. Solid products were separated by filtration from the oily fraction, from which methyl maleate was obtained by distillation. The solid material was subjected to fractional sublimation and methyl fumarate was first collected at 80° (100 mm.). Further sublimation at 100° (10 mm.) afforded methyl muconate, identified with an authentic sample of a *trans-trans* isomer of methyl muconate (m.p. 152°;  $\lambda_{\text{max}}^{\text{M}_{\text{OH}}}$  262.5  $\mu$  ( $\epsilon$  34,400)).<sup>5</sup> *Anal.* Calcd. for C<sub>8</sub>H<sub>10</sub>O<sub>4</sub>: C, 56.46; H, 5.92. Found: C, 56.49; H 5.84. The yield of methyl muconate was 38.5% and that of both the C<sub>4</sub> esters was 31.7%, based on palladium chloride.

In this reaction, the first step is presumed to be the coordination of 2 moles of acetylene to palladium as was assumed by Blomquist and Maitlis<sup>6</sup> in the case of diphenylacetylene. From this postulation it is reasonable to assume that the muconyl chloride, initially formed, should have a *cis-cis* form. By careful investigation of the reaction mixture using gas chromatography, the presence of a small amount of the *cis-cis* isomer was confirmed. We have found by using an authentic sample that the isomerization from the *cis-cis* to the *trans-trans* form in a benzene solution is particularly rapid in the presence of palladium chloride.

A mechanistic account of the reaction will be given in a forthcoming paper.

(5) J. A. Elvidge, R. P. Linstead, P. Sims, and B. A. Orkin, *J. Chem. Soc.*, 2235 (1950).

(6) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962).

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## BOOK REVIEWS

**Organic Reactions in Liquid Ammonia. Chemistry in Non-aqueous Ionizing Solvents. Volume 1, Part 2.** By HERCHEL SMITH. John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1963. 363 pp. 17 × 25 cm. Price, \$14.00.

Numerous reviews exist of limited aspects of organic reactions in liquid ammonia. This is the first book published which covers the subject as a whole. It is concerned with the properties of ammonia as a solvent for organic compounds, as a reagent with organic molecules, as a medium for the production of organic anions, and as a solvent for oxidation and reduction reactions. The most interesting section is that on reduction reactions involving alkali and alkaline earth metals. Dr. Smith has extensive research experience in this field, and presents an authoritative and balanced picture.

Literature surveys in a subject such as this are often very difficult, since the reactions are often incidental to some other aim and

are usually not appropriately indexed. Dr. Smith has performed a signal service in collecting 1388 references with coverage up to part of 1962; very few references of which the reviewer is aware are missing.

The treatment is on the whole a practical one, clearly aimed to provide information of use to the research chemist. The theoretical aspects are not neglected, however, since at least a working knowledge of theory is required to direct experiment in this field. Theoretical chemists may, in fact, be stimulated by the information presented to delve deeper into some interesting problems.

The book is well presented, divided clearly by numerous sub-headings, and adequately indexed with the references in alphabetical order of the initial author.

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