Communications TO THE EDITOR

Conversion of Phthalic Anhydride into Biphthalyl by Trialkyl Phosphites[1]

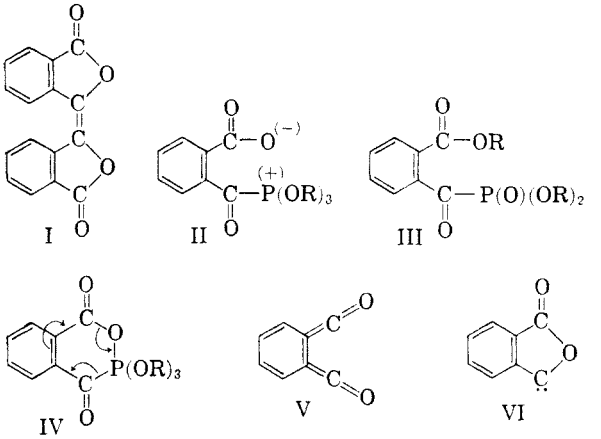
Sir:

We should like to report the conversion of phthalic anhydride into biphthalyl (I) by trialkyl phosphites, a novel reaction which may have wide synthetic applications.

A mixture of phthalic anhydride (74 g.) and *triethyl phosphite* (166 g.) was kept 37 hr. at reflux temperature, under nitrogen. From the mixture, 44 g. (65% yield) of biphthalyl (I),[2] m.p. 352–354°, separated on cooling. I, whose m.p. did not change upon recrystallization from xylene, was characterized by elemental analysis, saponification equivalent, and ultraviolet and infrared spectra; it was also compared with a sample of biphthalyl prepared from phthaloyl chloride in very low yield.[3]

The yield of biphthalyl (I) is considerably lower when *trimethyl phosphite* is used. Using 2 mol. of trimethyl phosphite per mol. of phthalic anhydride, approximately 74% of the latter was recovered unchanged after 20 hr. at reflux temperature. Biphthalyl (I) was obtained in *ca.* 5% yield and, in addition, dimethyl methylphosphonate, $CH_3P(O)(OCH_3)_2$, trimethyl phosphate $(CH_3O)_3PO$, and dimethyl phthalate were produced. No phosphite was left unchanged.

It is attractive to postulate an intermediate of type II in this reaction. From II, either an α-oxophosphonate ester[4] (III) or a species with pentacovalent phosphorus (IV) could be produced. The latter might be the precursor of biphthalyl *via* the diketene (V) and the carbene (VI). This, as well as other mechanistic schemes, is under study, and the sclope of the reaction of phosphite esters with anhydrides[4] is under investigation.



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(2) *Beilstein Handbuch der organishen Chemie*, 4th ed., Vol. 19, 176 (I 688), (II 192), J. Springer, Berlin, 1918.

(3) We are grateful to Dr. J. C. Sauer of E. I. du Pont de Nemours & Co. for a sample of biphthalyl prepared in 3% yield from unsymmetrical phthaloyl chloride. *Cf.* P. Karrer, W. Wehrli, E. Biederman, and M. dalla Vedova, *Helv. Chem. Acta*, **11**, 233 (1928).

(4) The formation of carboxylic esters and acylphosphonates from trialkyl phosphites and certain anhydrides has been reported. *Cf.* G. Kamai and V. A. Kukhtin *Akad. Nauk, S.S.S.R.*, Trudy 1-Oi Konferents, 1955, 91–97 *Chem. Abstr.*, **52**, 241 (1958).