

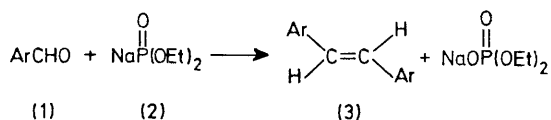
## New Olefin Synthesis from Carbonyl Compounds and Diethyl Sodiophosphonate

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**Summary** Reaction of aromatic aldehydes and phthalic and thiophthalic anhydrides with diethyl sodiophosphonate leads to *trans*-stilbenes, and to 3,3'-biphtalidyldiene and 3,3'-bis-(2-thiophthalidyldiene); reactions using *N*-methylisatoic anhydride and *N*-methylisatin as carbonyl compounds give *NN'*-dimethylisindigo.

A LARGE number of reactions of carbonyl compounds with dialkyl phosphite in the presence of base, such as sodium alkoxide and tertiary amines, are known to give  $\alpha$ -hydroxy phosphonic acid esters<sup>1</sup> but it has not been reported so far that these reactions also yield olefins. We now report a new olefin synthesis from relatively active carbonyl compounds and diethyl sodiophosphonate (**2**) in aprotic solvents.



- a; Ar = Ph  
 b; Ar = C<sub>6</sub>H<sub>4</sub>Me-*p*  
 c; Ar = C<sub>6</sub>H<sub>4</sub>Cl-*p*  
 d; Ar = C<sub>6</sub>H<sub>4</sub>OMe-*o*

Treatment of aromatic aldehydes (1) with (2) in benzene (or xylene) produces on heating *trans*-stilbenes (3) in good yields (Table).† The yields are temperature-dependent.

TABLE

Olefin synthesis from aldehydes (1) and NaP(O)(OEt)<sub>2</sub> (2).

Ar in (1)	Reaction conditions <sup>a</sup>			Yield of (3)/%
	Solvent	Temp/°C	Time/h	
Ph	C <sub>6</sub> H <sub>6</sub>	80	14	70
Ph	C <sub>6</sub> H <sub>6</sub>	130 <sup>b</sup>	7	63
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>6</sub>	130 <sup>b</sup>	11.5	85
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>m</i> -Xylene	139	5	72
<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>6</sub>	80	33.5	22

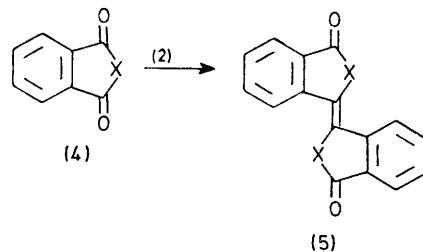
<sup>a</sup> 0.03 mol of (1), 0.03 mol of (2), and 50 ml of solvent. <sup>b</sup> The reaction was carried out in a sealed tube.

Similar syntheses of olefins from aromatic aldehydes and NaP(:O)Et<sub>2</sub> have been reported by Horner *et al.*<sup>2</sup> Reactions of phthalic (4a) (14 h) and thiophthalic (4b) (18 h) anhydrides with (2) in refluxing benzene give 3,3'-biphtalalidylidene (5a) (18%), m.p. 348–350 °C and 3,3'-bis-(2-thiophthalalidylidene), (5b) (44%), m.p. 330–331 °C, respectively.

† All compounds had the expected elemental analyses and spectral data.

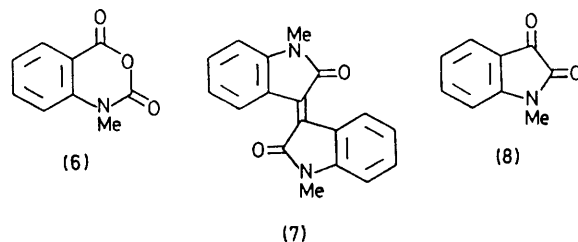
<sup>1</sup> See for examples, V. S. Abramov, *Doklady Akad. Nauk S.S.S.R.*, 1950, **73**, 487 (*Chem. Abs.*, 1951, **45**, 2855); A. L. Morrison and F. R. Atherton, B.P. 682,706 (*Chem. Abs.*, 1953, **47**, 11223f); V. S. Abramov, *Zhur. obshchei Khim.*, 1957, **27**, 169 (*Chem. Abs.*, 1957, **51**, 12878efg).

<sup>2</sup> L. Horner, P. Beck, and V. G. Toscano, *Chem. Ber.*, 1961, **94**, 1323.



- a; X = O  
 b; X = S

When *N*-methylisatoic anhydride (6) was treated with (2) in benzene for 15 h at 140 °C in a sealed tube, *NN'*-dimethylisoidingo (7), 37%, m.p. 277 °C,  $\delta$  (CDCl<sub>3</sub>) 3.20 (6H, s), 6.70–7.42 (6H, m), and 9.20 (2H, d), was obtained.



The product (7) was also obtained in 79% yield from *N*-methylisatin (8) and (2) under similar conditions.

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