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Reaction of Triethylphosphine with Dimethyl Acetylenedicarboxylate in the Presence of *p*-Chlorobenzaldehyde

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Synopsis. Reaction of triethylphosphine (**1**) with dimethyl acetylenedicarboxylate (**2**) in the presence of *p*-chlorobenzaldehyde gave dimethyl α-(*p*-chlorobenzoyl)-fumarate (**5**) and a bicyclic lactone (**6**). In the presence of water, reaction of **1** with **2** afforded dimethyl fumarate and triethylphosphine oxide.

Tertiary phosphines can add to acetylenic bonds.[1] The *1*:*1* adduct is considered to be a 1,3-dipole. Therefore, trapping of the 1,3-dipole with *p*-chlorobenzaldehyde was attempted, in order to check a possibility to prepare phosphorus-containing heterocycles.

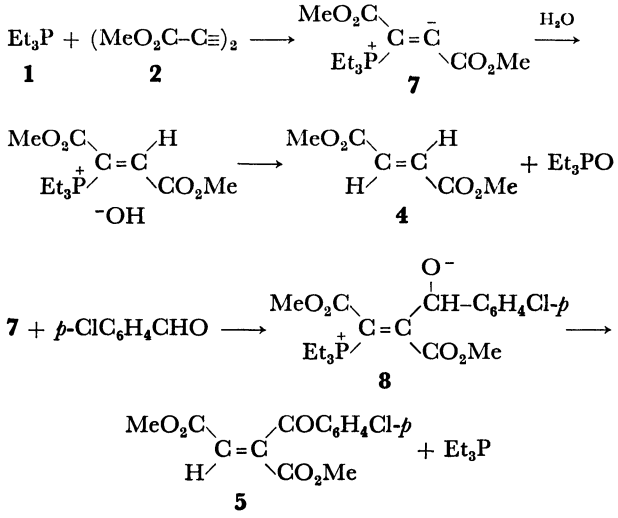
Dimethyl acetylenedicarboxylate (**2**) was added dropwise to a mixture of triethylphosphine (**1**) and *p*-chlorobenzaldehyde (**3**) in ether at room temperature. The reaction products were dimethyl fumarate (**4**) (1.3%), dimethyl α-(*p*-chlorobenzoyl)fumarate (**5**) (13%), a bicyclic lactone (**6**) (1.2%), and triethylphosphine oxide (58%).

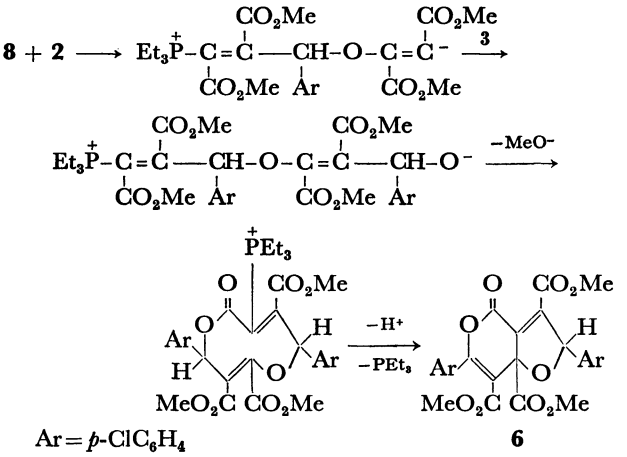
The structure of **5** was determined based on the spectral data, and the NMR data were essentially the same as those of dimethyl α-benzoylfumarate.[2] The structure of **6** was assigned by the spectral data. The carbonyl absorption band at 1760 cm^{-1} is in agreement with those of γ,δ-unsaturated δ-valerolactones.[3]

The methine proton at δ 6.50 is considerably broad, probably due to the presence of syn and anti protons to the bridgehead methoxycarbonyl group.

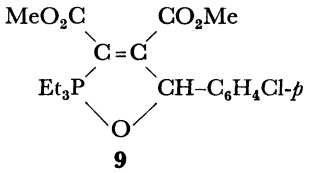
The formation of **4** is attributed to hydrolysis of a 1,3-dipolar intermediate (**7**) by moisture in the solvent, because the reaction of **1** with **2** in the presence of water gave 56% of **4** and 65% of triethylphosphine oxide. The formation of **4** exemplifies *trans* addition of **1** to **2** in accordance with *trans* structure of **5**.

The formation of **4**, **5**, and **6** is explained as follows.





Although the yield of **6** is low, similar result was also obtained when the reaction was carried out at 0 °C. The present result indicates that the 1,3-dipole (**7**) can not afford phosphorus-containing heterocycles such as **9**, probably because of *trans* relation in the cationic and anionic centers of **7**.



Experimental

Reaction of Triethylphosphine (1) with Dimethyl Acetylenedicarboxylate (2). a) In the presence of *p*-chlorobenzaldehyde (**3**): To a mixture of 2.33 g (19.7 mmol) of **1** and 13.3 g (95.1 mmol) of **3** in 20 ml of ether was added 5.23 g (36.8 mmol) of **2** in 40 ml of ether at room temperature over 6 h under nitrogen. Upon the addition of **2**, orange-red color developed in the solution. After evaporation of the solvent, the red tarry residue was chromatographed on silica gel. Elution with benzene recovered 0.372 g (7.1%) of **2** and 11.7 g (87.5%) of **3**. Fractions eluted with benzene–dichloromethane and dichloromethane–chloroform were rechromatographed on a silica gel dry column with dichloromethane to afford 1.35 g (13%) of **5**. Fractions eluted with dichloromethane–chloroform were rechromatographed on a silica gel dry column with dichloromethane to give 68 mg (1.3%) of **4**, mp 101.5—102.5 °C (lit,[4] 102.0 °C). Fractions eluted with chloroform were rechromatographed on a silica gel dry column with ether to give 0.239 g (1.2%) of **6**. Elution with methanol and distillation gave 1.52 g (58%) of triethylphosphine oxide. Red tar is polymerized **2**.

5: mp 79.5—80.5 °C (from ether); IR (KBr): 1730 (MeO-CO) and 1680 cm^{-1} (ArCO); NMR ($CDCl_3$): δ 3.65 (s, 3H, Me), 3.78 (s, 3H, Me), 7.08 (s, 1H, =CH–), 7.45, and 7.83

(A_2B_2, J_{HH}=8.4 Hz, 4H, C_6H_4); MS: *m/e* 282 (M^+, 3.7%) and 139 (ClC_6H_4CO, 100).

Found: C, 55.44; H, 3.73; Cl, 12.68%. Calcd for $C_{13}H_{11}O_5Cl$: C, 55.24; H, 3.92; Cl, 12.54%.

6: mp 203—205 °C (dec) (from acetone); IR (KBr): 1760 (sh) and 1740, 1660, and 1610 cm^{-1}; NMR ($CDCl_3$): δ 3.53 (s, 3H, Me), 3.87 (s, 3H, Me), 3.98 (s, 3H, Me), 6.50 (bs, 1H, CH), and 6.85—7.50 (m, 8H, $2C_6H_4$); MS: *m/e* 532 (M^+, 0.05 %) and 139 (ClC_6H_4CO, 100).

Found: C, 56.52; H, 3.10; Cl, 13.54%. Calcd for $C_{25}H_{18}O_9Cl_2$: C, 56.30; H, 3.40; Cl, 13.30%.

b) In the presence of water: To a mixture of 1.52 g (13.5 mmol) of **1** and 0.5 ml (27.8 mmol) of water in 30 ml of ether was added 2.11 g (27.8 mmol) of **2** in 20 ml of ether over 1.5 h at room temperature under nitrogen. Similar treatment afforded 1.17 g (56%) of **4** and 1.17 g (65%) of triethylphosphine oxide.

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