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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 $\bar{\bf 5}$ 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 $\bf 6$ 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.

$$\begin{array}{c} \operatorname{Et_{3}P} + (\operatorname{MeO_{2}C-C\equiv})_{2} \longrightarrow & \operatorname{MeO_{2}C} \\ \mathbf{1} \qquad \mathbf{2} & \operatorname{Et_{3}\overset{+}{P}} & \operatorname{C=\overset{-}{C}} \\ \operatorname{Et_{3}\overset{+}{P}} & \operatorname{CO_{2}Me} & \longrightarrow \\ & \operatorname{CO_{2}Me} & \operatorname{H} & \operatorname{MeO_{2}C} & \operatorname{H} \\ -\operatorname{CO_{2}Me} & \operatorname{H} & \operatorname{CO_{2}Me} & + \operatorname{Et_{3}PO} \\ & \operatorname{CO_{2}Me} & \operatorname{CO_{2}Me} & & \operatorname{CO_{2}Me} & \longrightarrow \\ & \operatorname{CO_{2}Me} & \operatorname{CO_{2}Me} & & \operatorname{CO_{2}Me} & \longrightarrow \\ & \operatorname{CO_{2}Me} & \operatorname{CO_{2}Me} & & \operatorname{CO_{2}Me} & \longrightarrow \\ & \operatorname{MeO_{2}C} & \operatorname{COC_{6}H_{4}Cl-p} \\ & \operatorname{Et_{3}\overset{+}{P}} & \operatorname{CO_{2}Me} & & \\ & \operatorname{MeO_{2}C} & \operatorname{COC_{6}H_{4}Cl-p} \\ & \operatorname{H} & \operatorname{CO_{2}Me} & & \\ & \operatorname{Et_{3}P} & \operatorname{COO_{2}Me} & & \\ & \operatorname{CO_{2}Me} & & & \\ & \operatorname{CO_{2}Me} & & & \\ & \operatorname{CO_{2}Me} & & & \\ & \operatorname{COO_{2}Me} & & & \\ & \operatorname{CO_{2}Me} & & \\ & \operatorname{CO_{2}Me} & & & \\ & \operatorname{CO_{2}Me} & & \\ & \operatorname{CO_{2}Me} & & & \\ & \operatorname{CO_{2}Me} & & \\ & \operatorname$$

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**.

$$C = C$$
 $C = C$
 $C = C$
 $CH - C_6H_4Cl-p$

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 (CDCl₃): δ 3.65 (s, 3H, Me), 3.78 (s, 3H, Me), 7.08 (s, 1H, =CH-), 7.45, and 7.83

 $(A_2B_2, J_{HH}=8.4 \text{ Hz}, 4H, C_6H_4)$; MS: m/e 282 (M+, 3.7%) and 139 (ClC₆H₄CO, 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 (CDCl₃): 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, 2C₆H₄); MS: m/e 532 (M⁺, 0.05 %) and 139 (ClC₆H₄CO, 100).

Found: C, 56.52; H, 3.10; Cl, 13.54%. Calcd for $C_{25}H_{18}$ - $O_{9}Cl_{2}$: 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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