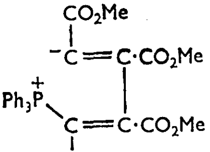
404. *The Adducts from Triphenylphosphine and Dimethyl Acetylenedicarboxylate.*

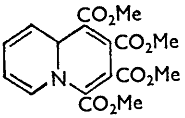
By A. W. Johnson and J. C. Tebby.

Various adducts from dimethyl acetylenedicarboxylate and triphenylphosphine have been characterised and structures for these and certain rearrangement products are suggested.

As an extension of our studies of the reaction of dimethyl acetylenedicarboxylate with various pyridines,[1] we have examined the corresponding reaction of the acetylenic ester with triphenylphosphine which is known to react easily with many unsaturated compounds.[2] In the reaction of triphenylphosphine and acetylenic esters the formation of bicyclic systems, as observed with the pyridine, is not possible but several new types of adduct have been recognised. Corresponding compounds have not been obtained from triphenylamine or triphenylarsine.

When triphenylphosphine was treated with dimethyl acetylenedicarboxylate in dry ether at −50° in an atmosphere of nitrogen there was formed a yellow unstable adduct, the analysis of which indicated that each molecule of triphenylphosphine had reacted with two of the acetylenic ester. At room temperature in air, the adduct became brown fairly rapidly but without loss of weight. By extraction with methanol the rearrangement product gave a second yellow solid which was extremely stable and was isomeric with its progenitor. Treatment of the unstable adduct with water, methanol, methyl iodide, or β-picoline also gave the stable isomer, and the first-formed adduct has therefore been provisionally formulated as the zwitterion (I). It will be recalled that Diels[3] assigned a


(I)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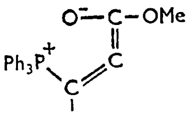
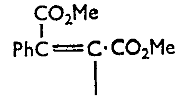

(III)


(IV)

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[1] Jackman, Johnson, and Tebby, *J.*, 1960, 1579.

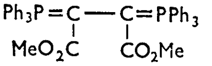
[2] Horner and Hoffmann, *Angew. Chem.*, 1956, **68**, 473.

[3] Diels, Alder, Kashimoto, Friedrichsen, Eckardt, and Klare, *Annalen*, 1932, **498**, 16.

similar structure to the first-formed adducts from pyridine and dimethyl acetylenedicarboxylate, but these compounds, which are much more stable than would be expected of a zwitterionic structure, recently have been reformulated [1,4] as the 9a(*H*)-quinolizines (*e.g.*, II). Horner and Hoffmann [2] have assigned a structure analogous to (I) to an adduct obtained from the reaction of triethylphosphine and dimethyl acetylenedicarboxylate, but no details of the properties or preparation of the adduct were disclosed. On the other hand, they suggested (III) as the structure of an adduct they obtained from triphenylphosphine and the acetylenic ester. We have not observed the formation of a 1 : 1 adduct (as in III) except in combination with carbon dioxide (see below, VI) and it is of interest that the decomposition products, dimethyl fumarate and triphenylphosphine oxide, of their adduct (III) with water correspond to those of our adduct (VI).

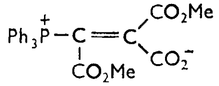
The structure (IV) was deduced for the stable yellow rearrangement product from the results of oxidation with hydrogen peroxide in acetic acid, which gave diphenylphosphinic and benzoic acid. The rearrangement of (I) to (IV) is thus formally analogous to the Stevens rearrangement,[5] but instead of the usual 1,2-shift, the present example is a 1,5-shift which is doubtless facilitated by the proximity of the charged centres.* Moreover, this appears to be the first example of this type of rearrangement involving phosphonium salts [6] and one of the few examples involving the migration of a phenyl group.[7] A third product from the oxidation appeared to be a lactone derived from the aliphatic chain but the low yield precluded complete identification of this substance.

The stable adduct (IV) was obtained directly from triphenylphosphine and dimethyl acetylenedicarboxylate when they reacted in boiling ether and this was the best method of preparation. It was noted during these preparations that after the addition of 0·5 mol. of the acetylenic ester to the triphenylphosphine, a thick yellow slurry was obtained which became less viscous as more acetylenic ester was added. This solid product was separated but it proved difficult to remove from it the small quantity of the adduct (IV) that was already present. Although satisfactory analyses were not obtained it appeared that this product is formed by the combination of two molecules of triphenylphosphine with each molecule of the acetylenic ester and accordingly (V) is suggested as a tentative structure. This product was decomposed rapidly by alcohols, yielding free

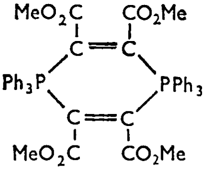


$Ph_3P{=}\underset{MeO_2C}{C}{-}\underset{CO_2Me}{C}{=}PPh_3$

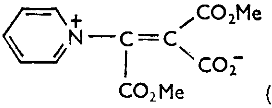
(V)



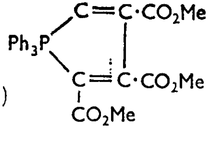
(VI)



(VII)



(VIII)



(Ia)

* We prefer to represent our adduct as having the charged structure (I), rather than the covalent structure (Ia), in order to provide a driving force for the migration of the phenyl group although we appreciate, as was pointed out by a Referee, that the rearrangement of (Ia) to (IV) would involve only a 1,2-shift.

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[4] Acheson and Taylor, *J.*, 1960, 1691.

[5] Stevens, *J.*, 1930, 2107 and later papers; Kantor and Hauser, *J. Amer. Chem. Soc.*, 1951, **73**, 4122.

[6] Cf. Wittig *et al.*, *Annalen*, 1953, **580**, 57; 1955, **594**, 1.

[7] Cf. Wittig and Stahnecker, *Annalen*, 1957, **605**, 69.

triphenylphosphine and a small quantity of the stable adduct (IV). Although compound (V) was stable in air at room temperature it could not be sublimed.

When triphenylphosphine reacted with dimethyl acetylenedicarboxylate in dry ether at −50° in an atmosphere of carbon dioxide, another pale yellow unstable adduct was obtained. This compound evolved carbon dioxide at 50° and yielded a very stable orange-coloured product. In view of the method of preparation and the analytical figures it is suggested that this unstable adduct is the zwitterion (VI), *i.e.*, the first-formed zwitterion obtained by reaction of equimolecular quantities of the reagents is stabilised by combination with carbon dioxide to give the internal salt of a half-ester of a malonic acid.

Treatment of this, second zwitterion with water caused the formation of triphenylphosphine oxide and dimethyl fumarate, a reaction which emphasises the relation of (VI) to the Wittig reagents.[8] However, most other reagents, *e.g.*, methyl iodide, β-picoline, and dimethyl acetylenedicarboxylate, caused the rearrangement of (VI) to the stable orange adduct which has been formulated as (VII). Because of its insolubility in suitable solvents and its lack of volatility an accurate determination of the molecular weight of this adduct has not been carried out, but oxidation with hydrogen peroxide in acetic acid gave triphenylphosphine oxide together with a small quantity of an unidentified aliphatic ester.

Compounds apparently analogous to (VI) were encountered in the study of the adducts of dimethyl acetylenedicarboxylate and tripropylphosphine as well as the pyridine bases,[1] where, however, the decomposition occurred at room temperature. These adducts are now formulated as (VIII), the carbon dioxide necessary for their formation having been derived from the surrounding acetone–carbon dioxide cooling bath! In this series, as nitrogen cannot assume the quinquecovalent state, the decomposition with liberation of carbon dioxide takes an alternative course and free pyridine is liberated together with some dimethyl fumarate.

EXPERIMENTAL

Ultraviolet absorption spectra refer to ethanolic solutions except where otherwise stated.

Reaction of Triphenylphosphine and Dimethyl Acetylenedicarboxylate in a Nitrogen Atmosphere at −50°.—Triphenylphosphine (1 g.) was dissolved in dry ether (25 c.c.) and placed in a specially constructed flask designed so that all operations, including filtration, could be conducted in an atmosphere of nitrogen, and then cooled to −50°. Dimethyl acetylenedicarboxylate (0·8 g.) in dry ether (5 c.c.) was added in a thin stream and after a short time a yellow solid separated. After 10 min., the flask was removed from the cooling-bath, and the yellow solid (I) was separated and dried *in vacuo* (Found: C, 66·4; H, 5·15. $C_{30}H_{27}O_8P$ requires C, 66·0; H, 5·0%), $\nu_{max.}$ (KBr disc) 695, 721, 751, 772, 793, 997, 1050, 1100, 1180, 1245, 1320, 1385, 1435, 1480, 1535, 1585, 1640, 1655, 1690, 1740, 1890, 1970, 2900, and 3400 cm.$^{-1}$. The ultraviolet absorption was not determined because of the insolubility of the sample in suitable solvents. This *product* was unstable and readily decomposed even at room temperature to the stable yellow adduct (see below), either in the dry state or in acetone or ethanolic solution.

Reaction of Triphenylphosphine and Dimethyl Acetylenedicarboxylate in Boiling Ether.—Triphenylphosphine (10 g.) in dry ether (50 c.c.) was added gradually to dimethyl acetylenedicarboxylate (10·6 g.) in dry ether (100 c.c.). The mixture was heated under reflux for 1 hr., then cooled, and the resulting solid was separated. After being washed with ether, it was air-dried and formed a yellow-brown powder (19·2 g.), m. p. 180—220°. This was boiled with methanol (250 c.c.) for 3 hr., the hot solution filtered, and the residue (6·4 g.), m. p. 248—250°, recrystallised by Soxhlet extraction from a thimble with methanol. The *product* (III) formed small yellow prisms, m. p. 253—255° (Found: C, 65·7; H, 5·0; P, 5·5; OMe 22·3; *M*, 520. $C_{30}H_{27}O_8P$ requires C, 66·0; H, 5·0; P, 5·7; OMe, 22·7; *M*, 547), $\lambda_{max.}$ 228 and 344 mμ (log ε 4·44 and 4·32 respectively), $\nu_{max.}$ 698, 721, 728, 747, 757, 778, 791, 866, 873, 902, 944, 968, 1019, 1042, 1089, 1112, 1138, 1190, 1218, 1255, 1321, 1396, 1440, 1449, 1484, 1496, 1533, 1589, 1665, 1698, 1715, 1746, 2850, 2945, 2990, and 3060 cm.$^{-1}$. The adduct was soluble in chloroform or dioxan, slightly soluble in acetone or alcohol and insoluble in water or light petroleum.

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[8] Trippett, " Advances in Organic Chemistry," Interscience, New York, 1960, Vol. I, p. 83.

The same stable adduct (0·6 g.) was obtained by keeping an ethereal solution of the above unstable adduct (I) (0·9 g.) at room temperature for 2 days. This transformation could also be achieved by heating the dry unstable adduct on the steam-bath or by treating it with water or with methyl iodide.

Oxidation of the Stable Yellow Triphenylphosphine Adduct.—The stable yellow adduct (8·5 g.) was heated with hydrogen peroxide (50 c.c.; 100-vol.) and glacial acetic acid (100 c.c.) on the steam-bath for 45 min. The whole was evaporated to dryness under reduced pressure, and acetone (20 c.c.) added to the residue. After cooling (refrigerator), the crystals of diphenylphosphinic acid [9] (1·6 g.) were separated, washed, and dried; they had m. p. and mixed m. p. 190—192°. The solvent was removed from the mother-liquors and the residue treated with methanolic 10% potassium hydroxide (20 c.c.). After the vigorous reaction had subsided, a further quantity of the reagent was added and the mixture heated under reflux for 1 hr. The methanol was distilled off and the residue treated with water (70—80 c.c.) and washed with chloroform (2 × 30 c.c.). The aqueous layer was acidified with concentrated hydrochloric acid and again extracted with chloroform (2 × 30 c.c.). This chloroform extract was washed and dried and then, after removal of the solvent, the cream-coloured solid residue was sublimed at 0·2 mm. and the crude sublimate (0·45 g.) extracted with hot water, to give benzoic acid (0·17 g.), m. p. 115°, raised to 121° after crystallisation, the identity of which was confirmed by its infrared spectrum. A further quantity of diphenylphosphinic acid (0·6 g.), m. p. 190—192°, was obtained by crystallisation from methanol of the sublimation residue; it had $\lambda_{\text{max.}}$ 224, 260, 265, and 270 mμ (log ε 4·15, 3·02, 3·11, and 2·91 respectively), $\lambda_{\text{infl.}}$ 295 mμ (log ε 2·25), $\nu_{\text{max.}}$ (KBr disc) 699, 703, 732, 760, 792, 867, 937, 968, 980, 1007, 1033, 1073, 1127, 1136, 1158, 1186, 1192, 1318, 1440, 1487, 1593, 1710, 3057, 3075, and 3583 cm.$^{-1}$.

Reaction of Triphenylphosphine and Dimethyl Acetylenedicarboxylate in a Carbon Dioxide Atmosphere at −50°.—Triphenylphosphine (1·5 g.) was dissolved in dry ether (30 c.c.) and cooled to −50°. Carbon dioxide was bubbled through the solution while dimethyl acetylenedicarboxylate (1 g.) in dry ether (5 c.c.) was added dropwise. The mixture was allowed to warm to room temperature and after 10 min. the colourless solid (V) (2·4 g.) was separated in an atmosphere of carbon dioxide, and washed with dry ether; it then had m. p. 78—80° (Found: C, 66·9; H, 5·1; P, 6·9. $C_{25}H_{21}O_6P$ requires C, 66·9; H, 4·7; P, 6·9%), $\nu_{\text{max.}}$ (KBr disc) 698, 724, 750, 757, 778, 862, 886, 925, 990, 1010, 1020, 1065, 1120, 1160, 1185, 1225, 1255, 1305, 1385, 1435, 1475, 1585, 1640, 1720, 2325, 2930, 3000, and 3400 cm.$^{-1}$. The ultraviolet absorption was not determined because of the instability of this *adduct* in solution. The solid evolved carbon dioxide rapidly at 50°; in a quantitative experiment 1 equiv. of carbon dioxide was evolved when the dry adduct was heated at 100° for $\frac{1}{2}$ hr. At room temperature the adduct could be preserved for one day in a desiccator.

This adduct (7·7 g.) was shaken with cold water (80 c.c.) and after 1 hr. colourless crystals had separated. After cooling, these were removed and dried. When the product (5·8 g.) was purified by sublimation, dimethyl fumarate (1·1 g.), m. p. 102—104°, was obtained as the sublimate and after crystallisation of the residue (4·6 g.) from aqueous ethanol, triphenylphosphine oxide (3·2 g.), m. p. and mixed m. p. 155—156°, was also isolated.

Preparation of the Stable Orange Adduct (VI).—Dimethyl acetylenedicarboxylate (3·5 g.) in ether (10 c.c.) was added to a solution of triphenylphosphine (5 g.) in dry ether (70 c.c.) cooled to −50° while a slow stream of carbon dioxide was bubbled through the solution. After 10 min. the solid product was separated, added to methyl iodide (20 c.c.), and heated under reflux for 30 min. The resulting solid (4·5 g.) was again separated, washed with methanol, and dried in air. Purification was effected by a preliminary extraction with boiling acetone (70 c.c.) for 2 hr. to remove impurities, and then by crystallisation of the residue (4·05 g.; m. p. 246—247°) by Soxhlet extraction with chloroform which gave small orange rods (2·25 g.), m. p. 266° (Found: C, 70·2; H, 5·3; P, 7·6; Loss on drying, 1·4. $C_{48}H_{42}O_8P_2,\frac{1}{2}H_2O$ requires C, 70·5; H, 5·3; P, 7·6; H_2O, 1·1%), $\lambda_{\text{max.}}$ (in $CHCl_3$) 337 and 435 mμ (log ε 3·6 and 3·6), $\nu_{\text{max.}}$ (KBr disc) 701, 724, 748, 762, 767, 792, 809, 901, 913, 943, 1006, 1030, 1082, 1106, 1114, 1167, 1206, 1235, 1278, 1319, 1362, 1442, 1489, 1517, 1572, 1590, 1707, 2840, 2902, 2946, 2993, 3020, 3063, and 3085 cm.$^{-1}$. This *adduct* was insoluble in light petroleum, ether, water, methanol, and acetone, and was slightly soluble in chloroform and dioxan.

Oxidation of the Stable Orange Adduct (VI).—The adduct (1 g.) was mixed with hydrogen

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[9] Michaelis and Götter, *Ber.*, 1878, **11**, 885.

peroxide (5 c.c.; 100-vol.) and glacial acetic acid (10 c.c.) and heated for 15 min. on the steam-bath. The product was evaporated to dryness and then heated at 100° under reduced pressure (water pump) to remove the last traces of solvent. The residue (0·6 g.) slowly crystallised and, by further sublimation or chromatography on an alumina column, pure triphenylphosphine oxide, m. p. and mixed m. p. 155—156°, was obtained. The infrared spectrum was identical with that of an authentic specimen.

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