A Synthesis of αβ-Unsaturated Aldehydes

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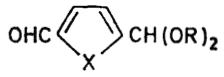
The synthesis and the use of 1,3-dioxan-2-ylmethyltriphenylphosphonium bromide (7) in the synthesis of αβ-unsaturated aldehydes is described.

In connection with extensions of our work on annulenones [1] we required an efficient method for the synthesis of various αβ-unsaturated aldehydes in the furan and thiophen series. The crossed aldol condensation usually gives low yields [2] and we were unable to extend it to 5-(diethoxymethyl)-2-furaldehyde (1). The method of Müller-Cunradi and Pieroh [3] has been used extensively for the synthesis of αβ-unsaturated aldehydes in carotenoid chemistry but it gave a poor yield when applied to 5-(dimethoxymethyl)thiophen-2-carbaldehyde (2).[4] The method of Trippett and Walker,[5] in which an aldehyde is treated with the resonance-stabilised ylide formylmethylenetriphenylphosphorane (3) to yield an

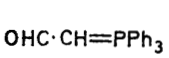
[1] T. M. Cresp and M. V. Sargent, *J.C.S. Perkin I*, 1973, 2961.
[2] A. A. Ponomarev and M. D. Lipanova, *Zhur. obshchei Khim.*, 1962, **32**, 2535.
[3] M. Müller-Cunradi and K. Pieroh, U.S.P. 2,165,962 (*Chem. Abs.*, 1939, **33**, 8210).
[4] V. I. Rogovik and Y. L. Gol'dfarb, *Khim. geterotsikl. Soedinenii, Akad. Nauk. Latv. S.S.R.*, 1965, 657 (*Chem. Abs.*, 1966, **64**, 14,156).
[5] S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1961, 2130.

αβ-unsaturated aldehyde and triphenylphosphine oxide appears attractive but has only been used in few cases.[5-7]



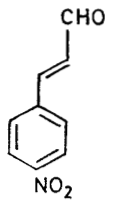
(1) X = O, R = Et

(2) X = S, R = Me



(3)

We found that Wittig reaction of 4-nitrobenzaldehyde with formylmethylenetriphenylphosphorane (3) (1·1 mol. equiv.) in boiling benzene for 24 h (the conditions used by Trippett and Walker [5]) gave 4-nitrocinnamaldehyde (4) in 67% yield; 8% of the starting material was recovered.



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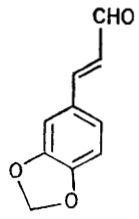

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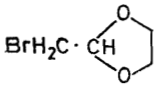

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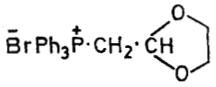
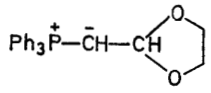


(7)

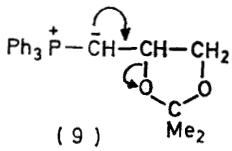
covered. The carbonyl group of 4-nitrobenzaldehyde is particularly prone to react with a nucleophile owing to the presence of the electron-withdrawing nitro-group. With the less reactive carbonyl system of piperonal the yield of 3,4-methylenedioxycinnamaldehyde (5) was only 17%, and 67% of the starting material was recovered. The resonance stabilisation of formylmethylenetriphenylphosphorane (3) thus limits the utility of this reagent to more reactive aldehydes. We therefore sought to extend the scope of this reaction by using a less stabilised ylide.

In agreement with Trippett and Walker [5] we were unable to obtain a crystalline triphenylphosphonium salt from reaction of bromo- or chloro-acetaldehyde diethylacetal with triphenylphosphine. However 2-(bromomethyl)-1,3-dioxolan [8] (6) smoothly gave 1,3-dioxan-2-ylmethyltriphenylphosphonium bromide (7), m.p. 191·5—193°. In order to facilitate the separation of the phosphine oxide produced in Wittig reactions Trippett and Walker [5] have described the use of *p*-*NN*-dimethylaminophenyldiphenylphosphine instead of triphenylphosphine in the preparation of phosphonium salts. However the dioxolan (6) did not form a crystalline phosphonium salt with the aminophenyldiphenylphosphine.

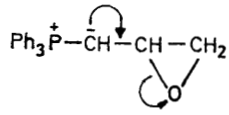
Since the ylide (8) carries a substituent in the position β to the phosphorus atom which is prone to undergo nucleophilic displacement, we chose to use the *in situ* method with lithium methoxide in methanol as base and *NN*-dimethylformamide or methanol as solvent for reaction of the ylide (8) with aldehydes. The ylides (9) and (10) [9] are thought to undergo such β-eliminations [10]



(8)

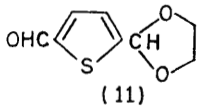


(9)



(10)

(arrows). When we attempted to generate the ylide (8) by the method of Greenwald *et al.*,[11] and carry out its reaction with aldehydes in a subsequent step the yields of products were significantly lower than those obtained by the *in situ* method. This suggests that β-elimination can also occur with the ylide (8). To ensure complete reaction of the substrate aldehyde we generally used 1·5 mol. equiv. of the phosphonium salt (7). This was sufficient, in the case of all the aldehydes studied



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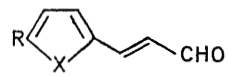
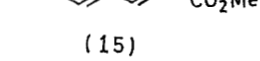


(12) R = Br, X = O

(13) R = CHO, X = O

(14) R = CHO, X = S



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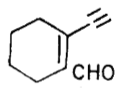

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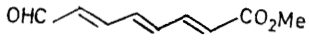

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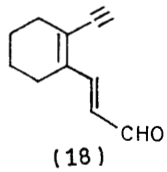

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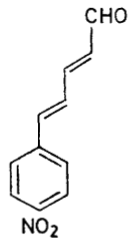


(19)

except piperonal, to ensure complete consumption of the starting material. In the case of piperonal 2·56 mol. equiv. of salt were required to ensure the optimum yield of 3,4-methylenedioxycinnamaldehyde (5).

[6] F. Dallacker, H. Pauling, and M. Lipp, *Annalen*, 1963, **663**, 58.

[7] H. Saikachi, Y. Taniguchi, and H. Ogawa, *Yakugaku Zasshi*, 1963, **83**, 582 (*Chem. Abs.*, 1963, **59**, 11,397).

[8] H. Bredereck, R. Gompper, R. Bangert, and H. Herlinger, *Chem. Ber.*, 1964, **97**, 827.

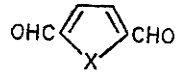
[9] F. Bohlmann and P. Herbst, *Chem. Ber.*, 1959, **92**, 1319.

[10] A. Maercker, *Org. Reactions*, 1965, **14**, 284.

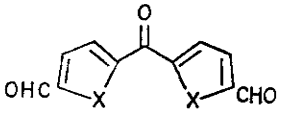
[11] R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, 1963, **28**, 1128.

The products of the Wittig reaction of the ylide (8) with aldehydes are the vinylogous αβ-unsaturated aldehydes, protected as their ethylene acetals. Trippett and Walker [5] observed that triphenylphosphine oxide was sometimes difficult to remove from the products of the reactions of aldehydes with formylmethylenetriphenylphosphorane. Our method offers the advantage that where necessary the triphenylphosphine oxide may be easily removed from the product acetals by chromatography over basic or neutral alumina. The acetals are less polar than their parent aldehydes. In general, however, the crude acetals were hydrolysed to the *trans*-αβ-unsaturated aldehydes, which were usually separated from the triphenylphosphine oxide by chromatography over silica gel.

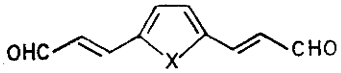
4-Nitrobenzaldehyde and piperonal gave the expected cinnamaldehydes (4) and (5) in 68 and 58% yields, respectively. Heptanal gave non-2-enal in 96% yield. In the five-membered heterocyclic series 5-bromo-2-furaldehyde, 5-(diethoxymethyl)-2-furaldehyde (1), and 5-(1,3-dioxan-2-yl)thiophen-2-carbaldehyde (11) gave the acrylaldehydes (12)—(14) in 58, 69, and 53% yields,



(20) X = O
(21) X = S

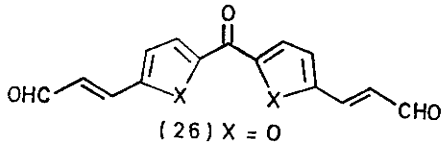


(22) X = O
(23) X = S

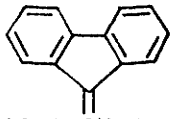


(24) X = O
(25) X = S

respectively. The method was also successful with unsaturated aldehydes. Thus methyl muconaldehydate (15), 1-ethynylcyclohex-2-enecarbaldehyde (16), and



(26) X = O
(27) X = S



(28) CH·CHO

4-nitrocinnamaldehyde (4) were converted into the aldehydes (17)—(19) in 51, 55, and 64% yields, respectively. The dialdehydes furan-2,5-dicarbaldehyde (20), thiophen-2,5-dicarbaldehyde (21), 2,2′-carbonyldifuran-5,5′-dicarbaldehyde (22), and 2,2′-thiocarbonyldifuran-5,5′-dicarbaldehyde (23) gave the products (24)—(27) in 60, 55, 76, and 64% yields, respectively.

Formylmethylenetriphenylphosphorane (3) does not react with ketones.[5] We have found that the ylide (8) with fluorenone under the standard conditions gave fluoren-9-ylideneacetaldehyde (28) in 21% yield. Some of the starting ketone (10%) was also recovered.

The ylide (8) is thus a versatile reagent for the synthesis of αβ-unsaturated aldehydes.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. Light petroleum was the fraction of b.p. 58—65° and was distilled from phosphorus pentoxide. *NN*-Dimethylformamide was stored for a prolonged period over 4 Å molecular sieves and then distilled onto 4 Å molecular sieves at 50—80 mmHg. Silica gel was B.D.H. 60—120 mesh. N.m.r. spectra were determined for solutions in deuteriochloroform at 60 MHz with a Varian A60A spectrometer, unless stated otherwise. For spectra determined at 90 MHz a Brüker Spectrospin instrument was used. Molecular weights were determined by mass spectrometry (Varian–M.A.T. CH-7 instrument operating at 70 eV).

Reaction of 4-Nitrobenzaldehyde with Formylmethylenetriphenylphosphorane (3).—Formylmethylenetriphenylphosphorane (3) [5] (1·00 g) and 4-nitrobenzaldehyde (453 mg) in dry benzene (40 ml) were heated under reflux under dry nitrogen for 24 h. The solvent was removed and the residue was preadsorbed from dichloromethane on silica gel and chromatographed over a column of silica gel with 5—20% ethyl acetate–light petroleum as eluant. Early fractions afforded the starting material (35·3 mg), which was followed by 4-nitrocinnamaldehyde (4) (353 mg). This formed pale yellow needles (from dichloromethane–light petroleum), m.p. 139—140·5° (lit.,[12] 141—142°); τ 0·19 (1H, d, $J_{CHO,\beta}$ 7·0 Hz, CHO), 1·68 and 2·25 (each 2H, AA′BB′, ArH), 2·42 (1H, d, $J_{\alpha\beta}$ 16·0 Hz, α-H), and 3·08 (1H, dd, $J_{\alpha\beta}$ 16·0, $J_{CHO,\beta}$ 7·0 Hz, β-H).

Reaction of Piperonal with Formylmethylenetriphenylphosphorane (3).—Formylmethylenetriphenylphosphorane (3) [5] (1·00 g) and piperonal (450 mg) in dry benzene (40 ml) were heated under reflux for 24 h. Work-up as before gave piperonal (301 mg) and 3,4-methylenedioxycinnamaldehyde (5) (92·2 mg), which formed pale yellow needles from dichloromethane–light petroleum, m.p. 83—84° (lit.,[13] 84—85°); τ (CCl_4) −0·20 (1H, d, $J_{CHO,\beta}$ 7·0 Hz, CHO), 2·72 (1H, d, $J_{\alpha\beta}$ 16·0 Hz, α-H), 2·90—3·29 (3H, m, ArH), 3·54 (1H, dd, $J_{\alpha\beta}$ 16·0, $J_{CHO,\beta}$ 7·0 Hz, β-H), and 3·98 (2H, s, CH_2).

2-(*Bromomethyl*)-1,3-*dioxolan* (6).—The method was adapted from that of Bredereck *et al.*[8] Ethanediol (35·5 g), bromoacetaldehyde diethyl acetal (109·8 g), and concentrated hydrochloric acid (0·5 ml) were heated and stirred for 9 h at 110—120° (bath) with the continuous removal of the liberated ethanol through a 10 cm Vigreux column. The crude product was fractionated under diminished pressure to afford the dioxolan (6) (80·6 g, 87%) as an oil, b.p. 82—84° at 27 mmHg (lit.,[8] 68—71° at 15 mmHg); τ (CCl_4) 4·87 (1H, t, C*H*·CH_2), 6·03 (4H, m, OCH_2), and 6·63 (2H, d, CH·C*H*$_2$).

1,3-*Dioxan*-2-*ylmethyltriphenylphosphonium Bromide* (7).—The dioxolan (6) (80·6 g) and triphenylphosphine (126 g) were heated on a steam-bath for 36 h. The cooled product was separated by filtration, washed well with dry ether, and

[12] L. Diehl and A. Einhorn, *Ber.*, 1885, **18**, 2335.
[13] H. Lohaus, *J. prakt. Chem.*, 1928, **119** [2], 235 (*Chem. Abs.*, 1928, **22**, 3886).

dried under vacuum to afford the *salt* (138·1 g, 67%). A sample crystallised from dichloromethane–dry ether formed prisms, m.p. 172—174° (raised to 191·5—193° on drying at 56° and 0·5 mmHg) (Found: C, 61·55; H, 5·1. $C_{22}H_{22}BrO_2P$ requires C, 61·55; H, 5·15%).

p-(*Dimethylamino*)*phenyldiphenylphosphine*.—The Grignard reagent was prepared by the method of Mendel [14] from 4-bromo-*NN*-dimethylaniline (20·0 g), magnesium (2·44 g), and dry tetrahydrofuran (150 ml) under dry nitrogen. Diphenylphosphinous chloride (22·0 g) in dry tetrahydrofuran (125 ml) was added over 1 h to the stirred Grignard reagent with cooling in ice–salt. The mixture was then stirred at room temperature for 1 h, treated with an excess of saturated ammonium chloride solution, and extracted exhaustively with benzene; the extract was washed with saturated brine, dried (Na_2SO_4), and evaporated. The residue crystallised from ethanol to form prisms (22·7 g, 74%) of the phosphine, m.p. 150—151° (lit.,[5] 152—153°).

5-(*Diethoxymethyl*)-2-*furaldehyde* (1).—A mixture of furan-2,5-dicarbaldehyde (20) [15] (5·00 g), triethyl orthoformate (6·4 g), and toluene-*p*-sulphonic acid (10 mg) in dry acetonitrile (27 ml) was heated on a steam-bath for 5 h. The cooled solution was diluted with ether and washed in turn with water, saturated aqueous sodium hydrogen carbonate, and saturated brine, dried (Na_2SO_4), and evaporated. The residue was distilled under diminished pressure and gave the acetal (1) (5·42 g, 68%) as a pale yellow oil, b.p. 91—94° at 0·6 mmHg; τ 0·33 (1H, s, CHO), 2·71 and 3·33 (2H, ABq, *J* 3·5 Hz, furan H), 4·40 (1H, s, methine H), 6·32 (4H, q, OCH_2), and 8·74 (6H, t, $O{\cdot}CH_2{\cdot}CH_3$).

5-(1,3-*dioxan*-2-*yl*)*thiophen*-2-*carbaldehyde* (11).—2-Bromo-5-(1,3-dioxan-2-yl)thiophen [16] (70·5 g) in dry ether (70 ml) was added dropwise over 15 min at −20° to a stirred solution of n-butyl-lithium (0·3 mol) in dry ether (300 ml) under dry nitrogen. After stirring at −20° for 40 min a solution of dry *NN*-dimethylformamide (22·0 g) in dry ether (50 ml) was added over 10 min. The mixture was stirred at −20 to −10° for a further 1 h and then an excess of saturated aqueous ammonium chloride was added. The mixture was diluted with water and exhaustively extracted with ether. The extract was washed with water (2 ×), and with saturated brine, dried (Na_2SO_4), and evaporated. The residue was fractionated under reduced pressure and afforded the acetal (11) (33·8 g, 62%) as a pale yellow oil, b.p. 134—138° at 2 mmHg or 118—120° at 0·8 mmHg; τ (CCl_4) 0·21 (1H, s, CHO), 2·40 and 2·87 (2H, ABq, *J* 3·5 Hz, furan H), 4·02 (1H, s, methine H), and 6·03 (4H, m, methylene H); M^+ 184.

General Procedure for Wittig Reactions.—Lithium methoxide [from lithium (15 mg atom for monoaldehydes, 30 mg atom for dialdehydes)] in dry methanol (50 ml) was added dropwise with stirring under dry nitrogen at 80—90° (bath) over 2·5—5 h to the aldehyde (10 mmol) and 1,3-dioxan-2-ylmethyltriphenylphosphonium bromide (7) (15 mmol for monoaldehydes, 30 mmol for dialdehydes) in dry *NN*-dimethylformamide (50 ml for monoaldehydes, 75 ml for dialdehydes). The salt was dried for 12 h at 56° at 0·05 mmHg immediately before use. After the addition of the base the mixture was stirred under dry nitrogen at 80—90° (bath) for a further 5—8 h (usually 5 h); the starting aldehyde could then no longer be detected by t.l.c. The mixture was then poured into water (600 ml) and extracted exhaustively with ether or pentane (depending on the solubility of the product). The extract was washed with saturated brine, dried (Na_2SO_4), and evaporated. The residue was stirred at room temperature with tetrahydrofuran (50 ml) and 10% hydrochloric acid (50 ml) for 2·5—3 h and the mixture was then diluted with water and extracted with ether. The extract was washed in turn with water, saturated aqueous sodium hydrogen carbonate, and saturated brine, dried (Na_2SO_4), and evaporated. The residue was preadsorbed from dichloromethane on silica gel and chromatographed over a column of silica gel with ethyl acetate–light petroleum of suitable polarity as eluant.

4-*Nitrocinnamaldehyde* (4).—This was obtained from 4-nitrobenzaldehyde and formed pale yellow needles (68%) (from dichloromethane–light petroleum), m.p. 139—140·5°, identical with that described before.

3,4-*Methylenedioxycinnamaldehyde* (5).—In order to obtain the optimum yield a larger excess of salt than usual was taken. Piperonal (10 mmol) was treated with the salt (7) (25·6 mmol); the product was obtained (58%) as pale yellow needles (from dichloromethane–light petroleum), m.p. 83—84°, identical with that described before.

Non-2-*enal*.—This was obtained from heptanal as a yellow oil (96%); τ 0·47 (1H, d, $J_{1,2}$ 7·5 Hz, CHO), 3·11 (1H, dt, $J_{2,3}$ 15·5, $J_{3,4}$ 6·5 Hz, 3-H), 3·89 (1H, dd with fine coupling on each peak, $J_{1,2}$ 7·5, $J_{2,3}$ 15·5 Hz, 2-H), 3·69 (2H, distorted t, 4-H), 8·62br (8H, 5-, 6-, 7-, and 8-H), and 9·09 (3H, distorted t, 9-H); 2,4-dinitrophenylhydrazone, m.p. 124—125° (lit.,[5] 126°).

2-*Bromo*-5-(β-*formylvinyl*)*furan* (12).—Obtained from 5-bromo-2-furaldehyde [17] this formed orange needles (58%) (from dichloromethane–light petroleum), m.p. 62—63° (lit.,[2] 62—63·5°); τ (CCl_4) 0·41 (1H, d, $J_{CHO,\beta}$ 7·0 Hz, CHO), 2·89 (1H, d, $J_{\alpha\beta}$ 16·0 Hz, α-H), 3·28 and 3·56 (2H, ABq, *J* 3·5 Hz, furan H), and 3·51 (1H, dd, $J_{\alpha\beta}$ 16·0, $J_{CHO,\beta}$ 7·0 Hz, β-H).

5-(β-*Formylvinyl*)-2-*furaldehyde* (13).—(A) *Reaction in* NN-*dimethylformamide*. This *product* was obtained from 5-(diethoxymethyl)-2-furaldehyde (1) in 69% yield by sublimation of the hydrolysate at 120° and 0·5 mmHg. It formed pale yellow prisms (from dichloromethane–light petroleum), m.p. 96—96·5° (Found: C, 63·9; H, 4·0%; M^+, 150. $C_8H_6O_3$ requires C, 64·0; H, 4·05%; *M*, 150); τ 0·22 (1H, s, 2-CHO), 0·24 (1H, d, $J_{CHO,\beta}$ 7·0 Hz, β-CHO), 2·61 (1H, d, $J_{\alpha\beta}$ 16·5 Hz, α-H), 2·64 and 3·02 (2H, ABq, furan H), and 3·24 (1H, dd, $J_{CHO,\beta}$ 7·0, $J_{\alpha\beta}$ 16·5 Hz, β-H).

(B) *Reaction in methanol*. Lithium methoxide [from lithium (260 mg)] in dry methanol (68 ml) was added dropwise over 30 min to a stirred solution of 5-(diethoxymethyl)-2-furaldehyde (1) (5·30 g) and the salt (7) (16·0 g) in dry methanol (150 ml) under dry nitrogen. After a further 1 h at room temperature the mixture was heated under reflux for 17 h. T.l.c. indicated that the starting aldehyde was still present. A further quantity of the salt (8·3 g) was added to the cooled solution, followed by lithium methoxide [from lithium (134 mg)] in dry methanol (41·6 ml) over 30 min. The solution was then heated under reflux for a further 18 h and cooled and the bulk of the solvent was removed under reduced pressure. The concentrate was diluted with water and extracted with ether and the extract was washed with water (2 ×) and saturated brine, dried (Na_2SO_4), and evaporated. The residue was preadsorbed

[14] A. Mendel, *J. Organometallic Chem.*, 1966, **6**, 97.
[15] G. Drechsler and K. Kopperschlaeger, East Ger.P. 26,542 (*Chem. Abs.*, 1964, **61**, 4315).
[16] S. Gronowitz, A. Biezas, and B. Mathiason, *Arkiv Kemi*, 1963, **21**, 265.
[17] Z. N. Nazarova, *Zhur. obshchei Khim.*, 1954, **24**, 575.

from dichloromethane on Woelm basic alumina (activity I) and chromatographed over a column of the same material (total 3 × 37 cm) with 10% ethyl acetate–light petroleum as eluant. Early fractions afforded a yellow oil (5·58 g) which was stirred for 2·5 h with ethanol (120 ml) and 5% hydrochloric acid (100 ml). Most of the ethanol was removed under reduced pressure and the residue was diluted with water and extracted with ethyl acetate. The extract was washed with saturated aqueous sodium hydrogen carbonate solution and saturated brine, dried (Na_2SO_4), and evaporated. The residue crystallised from dichloromethane–light petroleum to afford the aldehyde (13) as pale yellow prisms (2·50 g, 63%), m.p. 96—96·5°, identical with that described before.

5-(β-*Formylvinyl*)*thiophen*-2-*carbaldehyde* (14).—Lithium methoxide [from lithium (207 mg)] in dry methanol (71·5 ml) was added over 25 min to a stirred solution of the salt (7) (12·8 g) and 5-(1,3-dioxan-2-yl)thiophen-2-carbaldehyde (11) (5·0 g) in dry methanol (150 ml) under dry nitrogen. The mixture was then stirred at room temperature for 1 h, and heated under reflux for 4·5 h. The bulk of the solvent was removed from the cooled solution under reduced pressure. The concentrate was diluted with water and extracted with ether as before. The residue was preadsorbed from dichloromethane on Woelm neutral alumina (activity I) and chromatographed over a column of the same material (total 4 × 40 cm) with light petroleum (3·2 l) then 10% ethyl acetate–light petroleum as eluant; fractions of 200 ml were collected. Fractions 22—33 gave a yellow oil (3·846 g) which was hydrolysed as before to afford the aldehyde (14) (2·40 g, 53%) as yellow blades (from ethanol), m.p. 116—118° (lit.,[4] 120·5—121°); τ 0·07 (1H, s, 2-CHO), 0·31 (1H, d, $J_{CHO,\beta}$ 7·5 Hz, β-CHO), 2·41 (1H, d, $J_{\alpha\beta}$ 16·0 Hz, α-H), 2·26 and 2·56 (2H, ABq, J 3·5 Hz, thiophen H), and 3·37 (1H, dd, $J_{CHO,\beta}$ 7·5, $J_{\alpha\beta}$ 16·0 Hz, β-H).

Methyl 7-*Formylhepta*-2,4,6-*trienecarboxylate* (17).—Prepared from methyl muconaldehydate [18] (15), this formed pale yellow *plates* (51%) (from dichloromethane–light petroleum), m.p. 128—130° (Found: C, 65·4; H, 6·35%; M^+, 166. $C_9H_{10}O_3$ requires C, 65·05; H, 6·05%; M, 166); τ (90 MHz) 0·37 (1H, d, $J_{7,CHO}$ 7·5 Hz, CHO), 2·50—3·32 (4H, m, 3-, 4-, 5-, and 6-H), 3·73 (1H, dd, $J_{6,7}$ 14·5, $J_{7,CHO}$ 7·5 Hz, 7-H), 3·91 (1H, d, $J_{2,3}$ 15·2 Hz, 2-H), and 6·22 (3H, s, Me).

1-*Ethynyl*-2-(β-*formylvinyl*)*cyclohexene* (18).—Prepared from 2-ethynylcyclohex-1-enecarbaldehyde [19] (16), this formed yellow plates (55%) (from light petroleum), m.p. 57—58° (lit.,[20] 58—59°); τ 0·32 (1H, d, $J_{CHO,\beta}$ 8·0 Hz, CHO), 2·13 (1H, d, $J_{\alpha\beta}$ 15·5 Hz, α-H), 2·82 (1H, dd, $J_{\alpha\beta}$ 15·5, $J_{CHO,\beta}$ 8·0 Hz, β-H), 6·51 (1H, s, ethynyl H), 7·67 (4H, m, allylic H), and 8·29 (4H, m, homoallylic H).

5-(4-*Nitrophenyl*)*penta*-2,4-*dienal* (19).—Prepared from 4-nitrocinnamaldehyde (4), the *nitro-aldehyde* (19) formed yellow needles (64%) (from dichloromethane–light petroleum), m.p. 106—107·5° (Found: C, 65·05; H, 4·75; N, 6·6%; M^+, 203. $C_{11}H_9NO_3$ requires C, 65·0; H, 4·45; N, 6·9%; M, 203); τ (90 MHz) 0·33 (1H, d, J 7·8 Hz, CHO), 1·76 and 2·35 (each 2H, AA′BB′, ArH), 2·75 (3H, m, 3-, 4-, and 5-H), and 3·64 (1H, m, 2-H).

2,5-*Bis*-(β-*formylvinyl*)*furan* (24).—Obtained from furan-2,5-dicarbaldehyde (20),[15] the *dialdehyde* (24) formed yellow prisms (60%) (from dichloromethane–cyclohexane), m.p. 132—133° with slight sintering from 124° (Found: C, 67·9; H, 4·8%; M^+, 176. $C_{10}H_8O_3$ requires C, 68·2; H, 4·6%; M, 176); τ 0·74 (2H, d, $J_{CHO,\beta}$ 7·0 Hz, CHO), 3·11 (2H, d, $J_{\alpha\beta}$ 15·0 Hz, α-H), 3·45 (2H, s, furan H), and 3·83 (2H, dd, $J_{CHO,\beta}$ 7·0, $J_{\alpha\beta}$ 15·0 Hz, β-H).

2,5-*Bis*-(β-*formylvinyl*)*thiophen* (25).—Lithium methoxide [from lithium (593 mg)] in dry methanol (85 ml) was added dropwise over 5 h to a stirred solution of thiophen-2,5-dicarbaldehyde [21] (25) (4·00 g) and the salt (7) (36·6 g) in dry *NN*-dimethylformamide (250 ml) at 90° (bath) under dry nitrogen. The mixture was then stirred at room temperature for 6 h. The crude product, obtained in the usual way, was stirred with tetrahydrofuran (80 ml) and 10% hydrochloric acid (150 ml) for 1·5 h. The precipitate was filtered off, washed well with water, and dried under vacuum. It crystallised from dichloromethane–light petroleum as yellow needles (1·60 g), m.p. 190—192° (lit.,[4] 184°); τ ($CDCl_3$–Me_2SO) 0·22 (2H, d, $J_{CHO,\beta}$ 7·5 Hz, CHO), 2·11 (2H, d, $J_{\alpha\beta}$ 15·5 Hz, α-H), 2·38 (2H, s, thiophen H), and 3·37 (2H, dd, $J_{CHO,\beta}$ 7·5, $J_{\alpha\beta}$ 15·5 Hz, β-H). The aqueous filtrate was extracted with ethyl acetate and the extract worked up as usual. The residue was preadsorbed from dichloromethane on silica gel and chromatographed over a column of silica gel (total 4·5 × 53 cm) with 25% ethyl acetate–light petroleum as eluant (350 ml fractions were collected). Fractions 15—22 yielded 5-(β-formylvinyl)thiophen-2-carbaldehyde (14) (1·40 g, 29%), identical with that described before. Fractions 24—32 yielded the dialdehyde (25) (total yield 2·00 g, 55%).

Bis-5-(β-*formylvinyl*)-2-*furyl Ketone* (26).—This was prepared from 2,2′-carbonyldifuran-5,5′-dicarbaldehyde [1] (10 mmol) and the salt (7) (22 mmol) in 76% yield. It precipitated from the hydrolysis and was washed with water and dried under vacuum; it crystallised from aqueous acetone as yellow *prisms*, m.p. 196—197° (Found: C, 66·1; H, 3·85%; M^+, 270. $C_{15}H_{10}O_5$ requires C, 66·65; H, 3·75%; M, 270); τ ($CDCl_3$–Me_2SO) 0·43 (2H, d, $J_{CHO,\beta}$ 7·5 Hz, CHO), 2·29 (2H, d, $J_{\alpha\beta}$ 16·0 Hz, α-H), 2·48 and 2·96 (4H, ABq, J 3·5 Hz, furan H), and 3·44 (2H, dd, $J_{\beta,CHO}$ 7·5, $J_{\alpha\beta}$ 16·0 Hz, β-H).

Bis-5-(β-*formylvinyl*)-2-*thienyl Ketone* (27).—This was obtained in 64% yield from 2,2′-thiocarbonyldifuran-5,5′-dicarbaldehyde [1] (23) as for the analogue (26), and crystallised from acetone as yellow *needles*, m.p. 200—202° (Found: C, 59·85; H, 3·55%; M^+, 302. $C_{15}H_{10}O_3S_2$ requires C, 59·6; H, 3·35%; M, 302); τ [90 MHz; $(CD_3)_2SO$] 0·34 (2H, d, $J_{CHO,\beta}$ 7·5 Hz), 1·89 and 2·21 (4H, ABq, J 4·1 Hz, thiophen H), 2·03 (2H, d, $J_{\alpha\beta}$ 15·9 Hz, α-H), and 3·23 (2H, d, $J_{CHO,\beta}$ 7·5, $J_{\alpha\beta}$ 15·9 Hz, β-H).

Fluoren-9-*ylideneacetaldehyde* (28).—This was prepared from fluorenone in 21% yield. Some of the starting ketone (10%) was also recovered. The acetaldehyde formed orange-yellow needles (from light petroleum), m.p. 116—117° (lit.,[22] 116·5—117·5°); τ −0·82 (1H, d, J 8·0 Hz, CHO), 1·90—2·90 (8H, m, ArH), and 3·22 (1H, d, J 8·0 Hz, olefinic H).

We thank the Australian Research Grants Committee for financial support.

[3/1662 *Received*, 6th *August*, 1973]

[18] A. Funke and P. Karrer, *Helv. Chim. Acta*, 1949, **32**, 1016.
[19] G. M. Pilling and F. Sondheimer, *J. Amer. Chem. Soc.*, 1971, **93**, 1970.
[20] R. H. McGirk and F. Sondheimer, *Angew. Chem. Internat. Edn.*, 1972, **11**, 834.
[21] C. Sone, *Bull. Chem. Soc. Japan*, 1964, **37**, 1197.
[22] G. F. Hennion and B. R. Fleck, *J. Amer. Chem. Soc.*, 1955, **77**, 3253.