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A Useful Synthon: Acetylenedicarbaldehyde (But-2-ynedial)

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Summary The preparation of acetylenedicarbaldehyde (but-2-ynedial) (2) and its electrophilic properties towards some dienes are reported; the usefulness of the two aldehyde groups in the adducts obtained is exemplified by a Wittig reaction and the synthesis of a pyridazine.

ALTHOUGH 1,1,4,4-tetraethoxybut-2-yne (1) was prepared some years ago from triethyl orthoformate and an acetylene di-Grignard reagent,^{1,2} the corresponding free dialdehyde (2) could not be obtained under classical hydrolysis conditions³ and no synthetic method could be found to produce this four-carbon skeleton. We report here the first preparation of acetylenedicarbaldehyde (but-2-ynedial) (2). Dissolution of (1) in pure formic acid⁴ (1 g per 5 ml) quantitatively affords (2), as monitored by ¹H n.m.r. spectroscopy, after 2.5 h at 20 °C according to reaction (1).

$$\begin{array}{c} (\text{EtO})_2\text{CH}-\text{C=C-CH}(\text{OEt})_2 + 4 \ \text{HCO}_2\text{H} \rightarrow \\ (1) \\ \text{OCH-C=C-CHO} + 4 \ \text{HCO}_2\text{Et} + 2 \ \text{H}_2\text{O} \\ (2) \end{array} \tag{1}$$

The new compound could not be isolated in the pure state (evaporation under vacuum of the formolysis solution yields a liquid which readily polymerises); however, it was characterised in solution by spectroscopy: M^+ found 82.0054; calc. 82.0055; i.r. ν (CHCl₃)† 1675 cm⁻¹ (C=O); ¹H n.m.r. δ (CDCl₃) 9.83 (s, CHO).‡

In spite of its instability, (2) can be used for organic synthesis: solutions resulting from the formolysis of (1)reacted very easily with dienes (CH₂Cl₂ solution) affording



the expected Diels-Alder adducts. Thus, (3), (4), and (5) respectively were obtained from anthracene $(43\%; 20 \ ^{\circ}C)$ cyclopentadiene $(72\%; 0 \ ^{\circ}C)$, and cyclohexadiene $(75\%; 0 \ ^{\circ}C)$ [e.g; compound (3), yellow solid, m.p. 200 $\ ^{\circ}C$ (decomp.)

 \dagger This solution was obtained by dissolution in CHCl₃ of the residual liquid obtained after evaporation of the formolysis solution, and reaction with KHCO₃ and CaCl₂.

‡ Satisfactory high-resolution mass spectra were obtained for all new compounds.

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(CCl₄-hexane); i.r. ν (CHCl₃) 1678 (C=O); ¹H n.m.r. δ (CDCl₃) 10.02 (2 H, s, 2 CHO), 6.54 (8 H, m, ArH), and 5.40 (2 H, s, 2 CH bridgehead); ¹³C n.m.r. δ(CDCl₃) 185 (CHO), 157 (-C=), 143, 126, and 124 (arom.), and 48 p.p.m. (CH bridgehead)].[‡] It should be noted that (2) could not be conveniently obtained by MnO₂ oxidation⁵ of but-2-yne-1,4diol: only small traces of (3) were obtained when this reaction was performed in the presence of anthracene.

Acetylenedicarbaldehyde has interesting electrophilic properties similar to those of dimethyl acetylenedicarboxylate⁶ and, moreover, it has great synthetic potential resulting from the presence of the two aldehyde groups in the adducts produced; this is shown as follows by a Wittig reaction and the synthesis of a pyridazine.

Thus, the phosphorane Ph₃P=CH-CO₂Me reacts easily with (3) or (4) (room temperature, CHCl₃) to yield the

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- ⁴ Pure commercial grade formic acid was used; for formolysis of acetals see A. Gorgues, Bull. Soc. chim. France, 1974, 529.
 ⁵ R. K. Bentley, U. Graf, E. R. H. Jones, R. A. M. Ross, V. Thaller and R. A. Vere Hodge, J. Chem. Soc. (C), 1969, 689.
 ⁶ R. Fuks and H. G. Viehe, 'Chemistry of Acetylenes,' ed. H. G. Viehe, Marcel Dekker, New York, 1969, 425.

- ⁷ W. R. Vaughn, Chem. Rev., 1948, 447.

expected polyenes (6) (59%) and (7) (54%) [e.g. compound (6), white solid, m.p. $125 \,^{\circ}C$ (decomp.) (CCl₄-pentane); i.r. ν (CHCl₃) 1725 and 1705 (shoulder) cm⁻¹ (C=O); ¹H n.m.r. δ (CDCl₃) 7.83 and 6.28 (CH=CH, 2d, ³J 16 Hz, in agreement with an all trans configuration)].t

The reaction of hydrazine with vic-diformyl compounds is a classical method for pyridazine rings synthesis.^{3,7} When (3), dissolved in hot ethanol, is treated with an alcoholic solution of hydrazine hydrate, (8) precipitates within a few seconds as a white solid, yield 75%, m.p. 260 °C (ethanol); ¹H n.m.r. δ (CDCl₃) 9.27 (2 H, s, CH=N), 5.53 (2 H, s, CH bridgehead), and 7.27 (8 H, m, ArH).⁺

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