

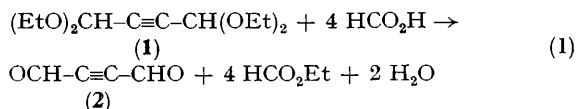
A Useful Synthone: Acetylenedicarbaldehyde (But-2-ynedial)

By ALAIN GORGUES* and ANDRÉ LE COQ

(Laboratoire de Synthèse Organique, Université de Rennes, 35042 Rennes Cedex, France)

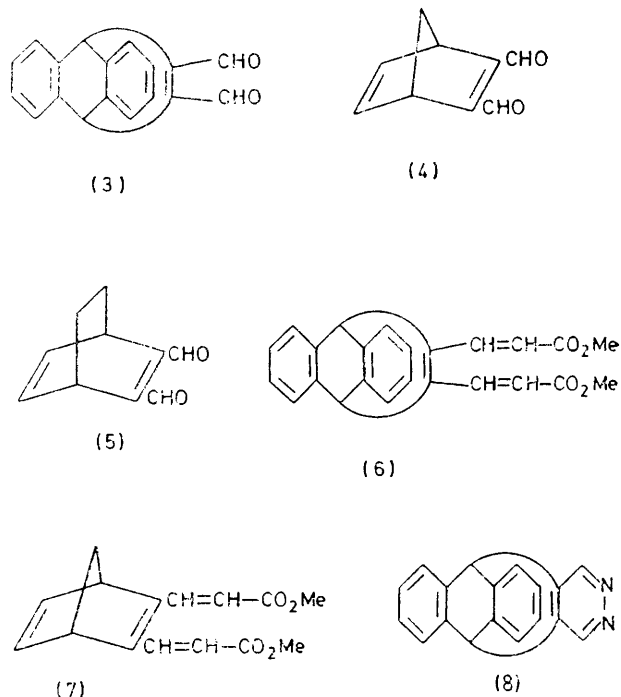
Summary The preparation of acetylenedicarbaldehyde (but-2-ynedial) (2) and its electrophilic properties towards some dienes are reported; the usefulness of the two aldehyde groups in the adducts obtained is exemplified by a Wittig reaction and the synthesis of a pyridazine.

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).



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. $\nu(\text{CHCl}_3)$ † 1675 cm^{-1} (C=O); ¹H n.m.r. $\delta(\text{CDCl}_3)$ 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 (CH_2Cl_2 solution) affording



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

† This solution was obtained by dissolution in CHCl_3 of the residual liquid obtained after evaporation of the formolysis solution, and reaction with KHCO_3 and CaCl_2 .

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

(CCl₄-hexane); i.r. $\nu(\text{CHCl}_3)$ 1678 (C=O); ¹H n.m.r. $\delta(\text{CDCl}_3)$ 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. $\delta(\text{CDCl}_3)$ 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-1,4-diol: 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

expected polyenes (6) (59%) and (7) (54%) [*e.g.* compound (6), white solid, m.p. 125 °C (decomp.) (CCl₄-pentane); i.r. $\nu(\text{CHCl}_3)$ 1725 and 1705 (shoulder) cm⁻¹ (C=O); ¹H n.m.r. $\delta(\text{CDCl}_3)$ 7.83 and 6.28 (CH=CH, 2 d, ³J 16 Hz, in agreement with an all *trans* configuration)].[‡]

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. $\delta(\text{CDCl}_3)$ 9.27 (2 H, s, CH=N), 5.53 (2 H, s, CH bridgehead), and 7.27 (8 H, m, ArH).[‡]

A. G. is grateful to Dr D. Martina for helpful and stimulating discussion.

(Received, 14th May 1979; Com. 507.)

¹ A. Moureu, *Ann. Chim.*, 1906, 550, 8(7).

² A. Wohl and B. Mylo, *Chem. Ber.*, 1912, 340, 45.

³ A. Wohl and E. Bernreuther, *Ann. Chem.*, 1930, 1, 481.

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.