Synthesis of Buta-1,2,3-trienes Possessing the 2-Pyridyl Unit, and a New Synthesis of P_2I_4

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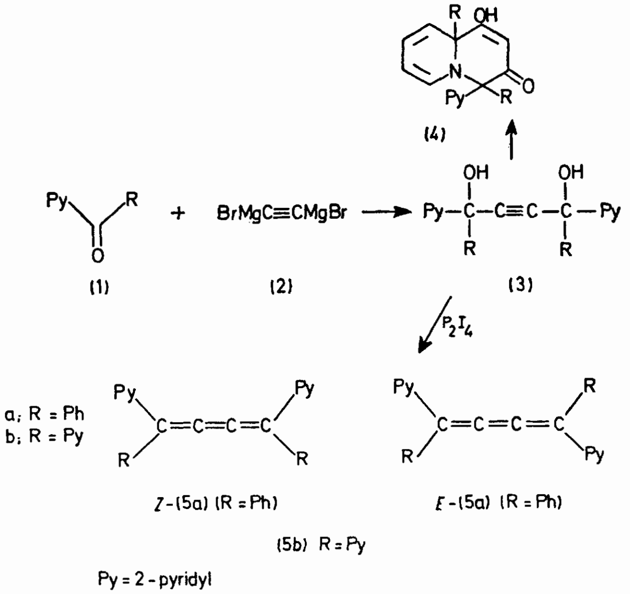
Summary The first examples of cumulenes which possess the 2-pyridyl unit have been prepared; isomeric 1,4-diphenyl-1,4-di-(2-pyridyl)butatrienes, as well as tetra-(2-pyridyl)butatriene, have been characterized.

During our investigation of multiheteromacrocycles,[1] we noted that cumulenes possessing pyridyl substituents had not been prepared. We herein report the first examples of buta-1,2,3-trienes which contain the 2-pyridyl unit.

Our attempts to prepare the dipyridylbutatriene (**5a**) by the standard reduction of the diol (**3a**) resulted in anomalous reactions even under the mildest conditions.[2] For example, when the diol (**3a**), prepared in $>90\%$ yield from (**1a**) and ethynediylbis(magnesium bromide),[3] was recrystallized from protic solvents or treated with dilute mineral acid, the pyridylquinolizinone (**4a**) was isolated ($>90\%$).[4] Attempts to reduce (**3a**) with $SnCl_2$ in Et_2O–HCl or with PBr_3 in pyridine also afforded (**4a**) along with traces of several previously proposed[4] intermediates.

Even though (**3a**) easily undergoes this acid catalysed rearrangement, the ready availability of these ynediols prompted us to find a mild reagent for this didehydroxylation. Recently, P_2I_4 has been used successfully for the generation of 1,4-dienes by a homo-1,4-elimination.[5] Although P_2I_4 had been prepared from elemental phosphorous and iodine in carbon disulphide,[6] a more convenient and less hazardous procedure (75% from PCl_3 and KI in



ether)† was used: m.p. 123—125 °C (sealed tube; highest lit.[6] m.p. 126—127 °C). Treatment of (**3a**) in anhydrous pyridine with P_2I_4 (recrystallized from CH_2Cl_2) resulted in instantaneous conversion into the cumulenes (**5a**) with total exclusion of (**4a**). The isomeric cumulenes were separated by preparative thick-layer chromatography [silica gel; 2 mm; cyclohexane–EtOAc (4:1)] with exclusion of light affording *E*-(**5a**)‡ as an orange powder [m.p. 141—143 °C (decomp., sealed tube); R_f 0·35; λ_{max} (C_6H_6) 430 (ϵ 26,000) and 276 (34,000) nm] and *Z*-(**5a**)‡ as yellow needles [m.p. 143—144 °C (decomp., sealed tube); R_f 0·30; λ_{max} (C_6H_6) 430 (ϵ 18,500) and 275 (12,200) nm]. Thermally, *Z*-(**5a**) was transformed into the thermodynamically stable *E*-isomer; photochemically, either pure *Z*- or *E*-(**5a**) isomerized to an approximately 1:1 mixture. The assignments of configuration for (**5a**) were similar to that for bis-(4-nitrobiphenyl-2,2′-diyl)butatriene[7a] and 1,4-diphenyl-1,4-di(2-nitrophenyl)butatriene.[7b]

Reaction of di-(2-pyridyl) ketone (**1b**) with (**2**) gave (32·5%) the extremely acid-labile tetrapyridylbutynediol (**3b**): m.p. 174—175 °C (from toluene), λ_{max} (C_6H_6) 275 nm (ϵ 13,400); ν_{max} (KBr) 3280, 1590, and 1565 cm^{-1}; δ ($CDCl_3$) 6·49 (OH, exchangeable with D_2O), 6·95—8·15 (m, py-H), and 8·47 (ddd, *J* 5·0, 1·8, and 0·9 Hz, 6′-py-H). Treatment of a solution of (**3b**) in pyridine with P_2I_4 at 0 °C gave the desired unstable cumulene (**5b**):‡ λ_{max} (C_6H_6) 407 (ϵ 600), 330 (6060), and 275 (6560) nm; δ ($CDCl_3$) 7·0—8·0 (m, py-H), 8·70 (ddd, *J* 5·0, 1·8, and 0·9 Hz, 6′-py-H). Although (**5b**) can be carefully chromatographed, as above, in the dark and under an inert atmosphere, all attempts to induce crystallization or to concentrate solutions have afforded complex mixtures of decomposition products. The notable instability of the cumulenes (**5a**) and especially (**5b**) emphasizes the diminished central double bond character when such butatrienes possess multiple electron-withdrawing substituents.

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† A slurry of KI (0·60 mol) in Et_2O (160 ml) was stirred vigorously under argon atmosphere while PCl_3 (0·2 mol) was added cautiously. After 12 h under reflux, solvent was removed under reduced pressure, and the residue was extracted with boiling CH_2Cl_2; the combined extracts were concentrated (*ca.* 100 ml) then cooled affording P_2I_4 (75—80%) as orange needles.

‡All new compounds gave satisfactory elemental analyses.

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