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Novel Catalytic Dimerization of t-Butylacetylene to *trans*-1,4-Di-t-butylbutatriene

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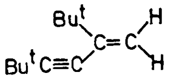
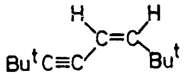
Summary With a catalytic amount of dihydridocarbonyltris(triphenylphosphine)ruthenium, t-butylacetylene stereoselectively dimerises to *trans*-1,4-di-t-butylbutatriene.

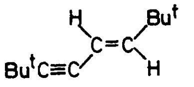
There are several reports on the dimerization of monosubstituted acetylenes to disubstituted vinylacetylenes by transition metal catalyst.[1] We now report a novel catalytic dimerization of t-butylacetylene to *trans*-1,4-di-t-butylbutatriene.

A benzene solution of t-butylacetylene was heated at 100 °C for several hours in the presence of a catalytic amount of dihydridocarbonyltris(triphenylphosphine)ruthenium. G.l.c. of the reaction mixture showed mainly five peaks in the range of the dimer fraction in a ratio of 6 : 1 : 1 : 4 : 88. The first three peaks could be assigned to isomeric vinylacetylenes (**1**), (**2**), and (**3**) based on i.r. and n.m.r. spectra. The last two peaks were assigned to isomeric butatrienes (**4a**) and (**4b**), as described below.[†]

Distillation of the reaction mixture gave a colourless liquid (**4b**) [*ca.* 50 catalytic turnovers per Ru atom, b.p. 80—83 °C at 20 mmHg] which could not be separated from small amounts of (**3**) and (**4a**). The ^1H n.m.r. spectrum of (**4b**) showed only two singlets at δ 1·10 (Me) and 5·47 (CH) and the ^{13}C n.m.r. spectrum ($CDCl_3$, rel. to Me_4Si) showed four resonances at δ 29·9 (q, *J* 125·8 Hz, Me), 35·0 (Me*C*), 118·2 (d, *J* 163·0 Hz, *C*H), and 160·0 (*C*) p.p.m. of which the last two are in fair agreement with spectra of the known butatrienes.[2] The u.v. spectrum [λ_{max} (EtOH) 293, 255, and 227 nm (ϵ 1,170, 29,200, and 13,600, respectively)] is very similar to those of aliphatic butatrienes such as tetra-t-butylbutatriene[3] and tetramethylbutatriene.[4]


(1)


(2)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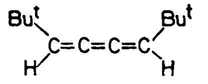
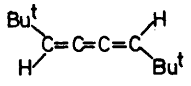

(4a)


(4b)

$Bu^tCHBrC{\equiv}CCHBrBu^t$
(5a)

$Bu^tCH{=}CBr{-}CBr{=}CHBu^t$
(5b)

Reaction of (**4b**) with bromine in chloroform provided the crystalline dibromide (**5**) (52%, m.p. 61—62 °C). The ^{13}C n.m.r. spectrum showed four resonances at δ 26·8 (q, *J* 126·3 Hz, Me), 36·8 (Me*C*), 50·5 (d, *J* 157·5 Hz, *C*HBr), and 85·6 (*C*), and suggested the acetylenic dibromide structure (**5a**) rather than the isomeric 2,3-dibromobutadiene structure (**5b**) which is known to be the common product in halogenation of butatrienes.[5] Non-formation of (**5b**) may be due to steric hindrance of the bulky t-butyl groups.

[†] When $[RuH_2(PPh_3)_4]$ and $[RuH(CO_2Me)(PPh_3)_3]$ were used as catalysts, (**1**), (**2**), (**3**), and (**4b**) were obtained in a ratio of 43 : 16 : 6 : 35 and 50 : 28 : 16 : 6, respectively. Compound $[RhCl(PPh_3)_3]$ is known to give (**3**) almost exclusively (ref. 1b).

When (**4b**) was distilled at ordinary pressure, an equilibrium mixture of (**4a**) and (**4b**) was obtained without any appreciable decomposition [b.p. 185 °C, (**4b**) : (**4a**) *ca.* 1·25 : 1]. The ^{1}H n.m.r. spectrum of the distillate shows resonances due to (**4a**) at δ 1·08 (s, Me) and 5·51 (s, CH) in addition to those due to (**4b**).

For the determination of the stereochemistry, (**4b**) was treated with η-cyclopentadienylbis(triphenylphosphine)-cobalt[6] at room temperature to give an air-stable red-brown crystalline compound of the formula [Co(η-C_5H_5)(Bu^{t}CH=C=C=CHBu^t)(PPh_3)] (**6**) [49%, m.p. 147·5 °C (decomp.)]. The ^{1}H n.m.r. spectrum showed the existence of two kinds of t-butyl groups (δ 1·10 and 1·34) and vinylic protons (δ 5·63 and 6·68) along with cyclopentadienyl protons and phenyl protons which indicates *trans*-configuration of the butatriene species.[7] Oxidation of (**6**) by ceric ammonium nitrate regenerates (**4b**) which is accompanied by the isomer (**4a**) (15%). Even if an equilibrium mixture of (**4a**) and (**4b**) were used for the reaction, only (**6**) was formed. Failure to obtain a *cis*-butatriene cobalt complex is undoubtedly due to steric factors‡ and this may explain why the present catalytic reaction proceeds stereoselectively. A suggested reaction pathway could involve initial formation of a t-butylvinylideneruthenium intermediate and subsequent coupling of the 't-butylvinylidene' species in the co-ordination sphere of ruthenium. Recent isolation of a phenylvinylidenemanganese complex from the reaction of [Mn(η-C_5H_5)$(CO)_2$(thf)] (thf = tetrahydrofuran) with phenylacetylene[8] is of interest in this connection.

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‡ Attack of the cobalt atom on the side of the butatriene near to the t-butyl groups is hindered. The attack on the reverse side also would not give a corresponding complex because of steric hindrance.

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[7] Bonding at the central double bond was assumed, which is true in the case of the tetraphenylbutatrienetetracarbonyliron: K. K. Joshi, *J. Chem. Soc.* (*A*), 1966, 598. Analogous structure was given for [Co(η-C_5H_5)(Ph_2C=C=C=CPh_2)(PPh_3)]: P. Kim and N. Hagihara, *Mem. Inst. Sci. Ind. Res., Osaka University*, 1967, **24**, 133.

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