Vinyl Cations in Organic Synthesis. Part 2.[1] A Novel Synthesis of Methylene-1*H*-indenes (Benzofulvenes) by Cyclisation of Phenyl-substituted But-1-en-3-ynes

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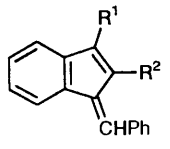
A series of phenyl-substituted but-1-en-3-ynes has been prepared and their reactivity toward acid-catalysed cycloisomerisation investigated. In boiling dichloromethane or 1,2-dibromoethane, in the presence of a catalytic amount of methanesulfonic acid, 1,1,2,4-tetraphenylbutenyne, 1,1,4-triphenylbutenyne, and (*Z*)-1,2,4-triphenylbutenyne afforded 1-benzylidene-2,3-diphenyl-1*H*-indene, (*E*)- and (*Z*)-1-benzylidene-3-phenyl-1*H*-indene and (*E*)- and (*Z*)-1-benzylidene-2-phenyl-1*H*-indene, respectively, in fair to good yields. Under the same conditions, (*E*)-1,2,4-triphenylbutenyne and (*E*)- and (*Z*)-1,4-diphenylbutenyne did not afford cyclisation products and were recovered unchanged. The cycloisomerisation reaction is rationalised in terms of formation of vinyl cation intermediates by exclusive protonation at the 4-position of the butenyne chain followed by intramolecular electrophilic attack on a suitably located and orientated phenyl nucleus in the 1-position.

As an extension of our work on the electron-transfer reduction of phenyl-substituted indenes,[2] we have focused our attention on indenyl substrates having both an *endo*- and an *exo*-cyclic double bond, namely phenyl-substituted methylene-1*H*-indenes (benzofulvenes) **1**.

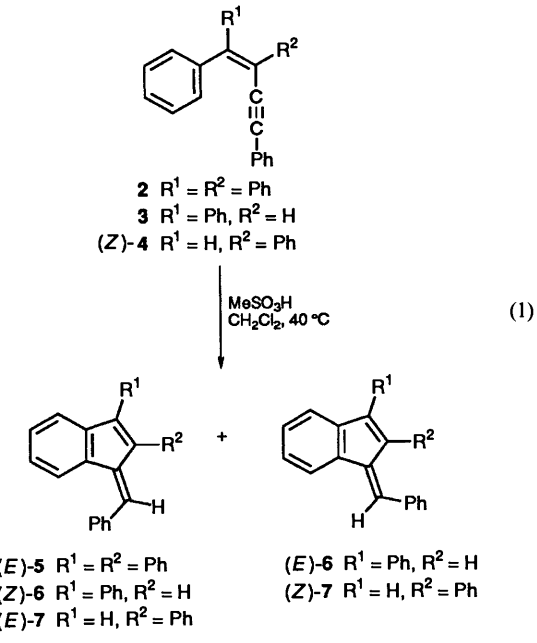


R^1, R^2 = H, Ph

As a general synthetic approach to these substrates, we took into consideration a cycloisomerisation based on an intramolecular electrophilic attack on a suitably located phenyl nucleus by an unsaturated cationic centre.[3] This type of reaction has been shown, indeed, to afford easily a series of unsaturated five-membered cyclic derivatives, such as benzo[*b*]furans,[4] *N*-substituted indoles,[5] benzo[*b*]thiophenes,[6] benzo[*b*]thiophene 1,1-dioxides,[7] indenes[8] and indenones.[9]

Therefore, we studied the behaviour of various phenyl-substituted but-1-en-3-ynes under acidic conditions. We found that 1,1,2,4-tetraphenylbutenyne **2**, 1,1,4-triphenylbutenyne **3** and, less readily, (*Z*)-1,2,4-triphenylbutenyne **4** when treated with a catalytic amount of methanesulfonic acid in refluxing dichloromethane (or other inert solvent) afforded the corresponding phenyl-substituted methylene-1*H*-indenes **5**, **6** and **7** [eqn. (1)].

This reaction represents a new synthetic approach to the benzofulvenic system.[10] As a matter of fact, other acid-catalysed cycloisomerisations probably occurring *via* vinyl cations have been reported, in which benzofulvenes were obtained from tetraarylbutatrienes[11] and from *o*-bis(phenylethynyl)benzenes.[12] On the other hand, photocyclisation of a large series of 1,4-diarylbutenynes was shown to afford exclusively six-membered rings.[13]



2 $R^1 = R^2$ = Ph
3 R^1 = Ph, R^2 = H
(*Z*)-**4** R^1 = H, R^2 = Ph

(*E*)-**5** $R^1 = R^2$ = Ph
(*Z*)-**6** R^1 = Ph, R^2 = H
(*E*)-**7** R^1 = H, R^2 = Ph

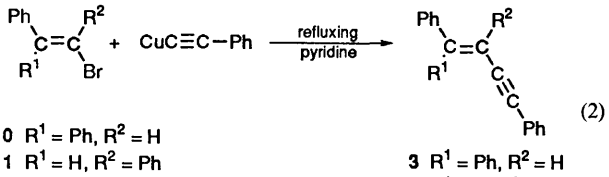
(*E*)-**6** R^1 = Ph, R^2 = H
(*Z*)-**7** R^1 = H, R^2 = Ph

(1)

Results and Discussion

Preparation of Phenyl-substituted But-1-en-3-ynes.—Two synthetic routes were followed for the synthesis of the butenynes **2**–**4**. Compounds **2** and (*Z*)-**4** were prepared by dehydration of the acetylenic alcohol obtained by the Grignard reaction of phenylethynylmagnesium bromide with the appropriate 2-phenyl-substituted acetophenones **8** and **9** (Scheme 1).

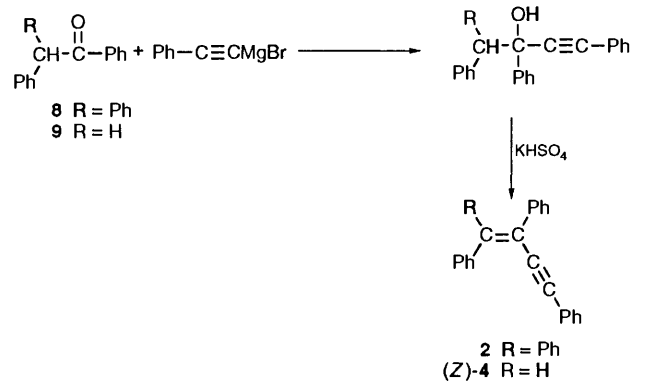
Butenynes **3** and (*E*)-**4** were prepared by the coupling reaction of copper(I) phenylacetylide with 2-bromo-1,1-diphenylethene **10** and (*E*)-1-bromo-1,2-diphenylethene **11**, respectively, in refluxing pyridine according to the method reported by Burdon *et al.*[14] [eqn. (2)].



10 R^1 = Ph, R^2 = H
11 R^1 = H, R^2 = Ph

3 R^1 = Ph, R^2 = H
(*E*)-**4** R^1 = H, R^2 = Ph

(2)



Scheme 1

In order to confirm the stereoselectivity of this coupling reaction, the known (*E*)- and (*Z*)-1,4-diphenylbutenynes[15] **12** were prepared from (*E*)- and (*Z*)-2-bromostyrenes **13**, respectively. The complete stereoselectivity observed made it possible to assign the *E*-configuration to the previously unknown 1,2,4-triphenylbutenyne **4** obtained by the same method and hence the *Z*-configuration to 1,2,4-triphenylbutenyne **4** prepared according to Scheme 1.

Acid-catalysed Cyclisation of Phenyl-substituted Butenynes.—The cyclisation was carried out by allowing all the prepared butenynes to react with a catalytic amount of methanesulfonic acid in boiling dichloromethane or, in the case of (*Z*)-**4**, in boiling 1,2-dibromoethane. Reaction conditions and yields of the benzofulvenes obtained are reported in Table 1.

Butenyne **2** afforded 1-benzylidene-2,3-diphenyl-1*H*-indene **5** as the sole product in nearly quantitative yield. This corresponded to the only isomer as yet reported in the literature; the *E*-configuration to this isomer was recently assigned on the basis of its crystalline structure.[16]

Butenyne **3** gave a mixture of (*E*)- and (*Z*)-1-benzylidene-3-phenyl-1*H*-indene **6**. Fractional recrystallisation of this mixture permitted us to isolate and characterise a previously unknown configurational isomer of **6**, having m.p. 145–146 °C, in addition to the known isomer[17] with m.p. 77 °C and, therefore, to assign configurations. This assignment was mainly based on the fact that, owing to a *trans*-stilbene-like chromophore, the *E*-isomer has the longest wavelength band in the UV spectrum shifted bathochromically with respect to the *Z*-isomer, in analogy with the findings of Whitlock *et al.*[12] for the isomeric benzofulvenes **7**. The *E*-configuration was, therefore, assigned to the isomer with m.p. 77 °C.

Butenyne (*Z*)-**4** afforded a mixture of (*E*)- and (*Z*)-1-benzylidene-2-phenyl-1*H*-indene **7** which was separated by fractional recrystallisation and the individual isomers recognised by comparison with the data reported by Whitlock *et al.*,[12] to whom we refer for an ample discussion of the assignment of configuration.

As reported in Table 1, butenynes (*E*)-**4** and (*E*)- and (*Z*)-**12** gave no cyclisation product and were recovered practically unchanged even after prolonged reaction times. No acid-catalysed isomerisation around the double bond was observed.

General Remarks.—The results obtained may be rationalised, in analogy with previous work,[4–8] in terms of formation of vinyl cation intermediates **14** by protonation of the triple bond of the substrates in the 4-position, subsequent intramolecular attack of the positive centre on the 1-phenyl nucleus located in the *cis*-position and final proton loss (Scheme 2).

The exclusive protonation at the 4-position of the butenyne system to afford cation **14** is a further example of the well known behaviour of conjugated vinylacetylenes, which were shown to give, upon electrophilic attack, vinyl cations stabilised by an α-vinyl group.[18]

To the best of our knowledge, however, this has been observed to date only with vinylacetylene and some alkyl-substituted homologues. Our results indicate that this behaviour is followed also by phenyl-substituted substrates, where the presence of the phenyl groups, independently of their number and position, does not affect the regioselectivity of the protonation reaction. On the other hand, the number and position of the phenyl groups along the butenyne chain have a significant effect on the rate of cyclisation. In fact, the reactivity shown by the substrates undergoing cyclisation follows the order: **2** > **3** ≫ (*Z*)-**4**. This trend is presumably related to steric interactions between the phenyl groups, which allow the molecule to assume the most favourable conformation to undergo cyclisation. As a matter of fact, where there is no interaction between the phenyl groups in the 1- and/or 2-position [as in the case of (*Z*)-**12**] or where the phenyl group in the 1-position is *trans* to the acetylenic moiety [as in the case of (*E*)-**4** and (*E*)-**12**] cyclisation does not occur.

Experimental

M.p.s are uncorrected. ^{1}H NMR spectra of $CDCl_3$ solutions were recorded with a Varian EM-360 A spectrometer operating at 60 MHz. The chemical shifts are reported in ppm downfield from internal Me_4Si. *J* Values are given in Hz. IR spectra were recorded with a Perkin-Elmer 983 spectrometer. UV spectra of heptane solutions were recorded with a Perkin-Elmer 402 spectrophotometer. Elemental analyses were performed at the Microanalytical Laboratory of the Dipartimento di Chimica Organica, Padova.

Materials.—Solvents were purified and dried following standard procedures. In the column chromatographies silica gel (Merck, 70–230 mesh) and light petroleum (b.p. 40–60 °C) were used. Ether refers to diethyl ether. Phenylacetylene and 2-phenylacetophenone **9** were commercial products (Aldrich) and were purified by distillation and recrystallisation, respectively. 2,2-Diphenylacetophenone[19] **8**, 2-bromo-1,1-diphenylethene[20] **10**, (*E*)-1-bromo-1,2-diphenylethene[8b] **11**, (*E*)- and (*Z*)-2-bromostyrenes[21] **13** and copper(I) phenylacetylide[22] were prepared following literature methods.

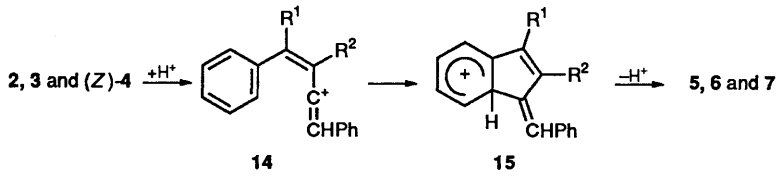
1,1,2,4-Tetraphenylbut-1-en-3-yne **2** was prepared according to the procedure reported in the literature[23] with a minor modification ($KHSO_4$ at 120 °C instead of 20% aqueous H_2SO_4 in the final dehydration step, according to Scheme 1) in 75% yield based on 2,2-diphenylacetophenone **8**, white crystals, m.p. 136 °C (from EtOH) (lit.,[23] 136 °C); δ_H 6.80–7.70 (20 H, m, Ph).

1,1,4-*Triphenylbut*-1-*en*-3-*yne* **3**.—To a stirred solution of 2-bromo-1,1-diphenylethene **10** (3.6 g, 13.9 mmol) in dry pyridine (40 cm^3), under a nitrogen atmosphere, copper(I) phenylacetylide (2.5 g, 15.2 mmol) was added at once, and the mixture was heated and kept at reflux for 48 h. After cooling, the black mixture was poured into conc. hydrochloric acid (80 cm^3) and crushed ice, and the resulting mixture extracted with ether (200 cm^3). The extract was washed with aqueous sodium hydrogen carbonate and water, dried ($CaCl_2$) and evaporated to dryness under reduced pressure. Column chromatography of the residue on silica gel with light petroleum as eluent afforded first diphenylbutadiyne, m.p. 86–87 °C (0.2 g, 10%) (lit.,[24] m.p. 87 °C). Further elution with light petroleum–benzene (9:1) afforded the *title compound* **3** (1.8 g, 46%) as white crystals (from absolute EtOH), m.p. 104–105 °C (Found: C, 94.35; H, 5.8. $C_{22}H_{16}$ requires C, 94.25; H, 5.75%); ν_{max}(KBr)/cm^{-1} 2190 (C≡C); δ_H 6.22 (1 H, s, vinylic) and 7.20–7.65 (15 H, m, Ph).

Table 1 Results of the cyclisation reaction[a]

Compound	Solvent	T/°C	t/h	Products	Total yield (%)	(E):(Z) ratio[b]
2	CH_2Cl_2	40	6	**5**	93	
3	CH_2Cl_2	40	90	(*E*)- and (*Z*)-**6**	61	3:1
(*E*)-**4**	CH_2Cl_2	40	168	(*E*)- and (*Z*)-**7**	10	n.d.
(*E*)-**4**	CH_2Cl_2	105[c]	168	(*E*)- and (*Z*)-**7**	25	n.d.
(*E*)-**4**	1,2-Dibromoethane	132	146	(*E*)- and (*Z*)-**7**	75	9:1
(*Z*)-**4**	1,2-Dibromoethane	132	146	*d*		
(*E*)-**12**	CH_2Cl_2	40	168	*e*		
(*Z*)-**12**	CH_2Cl_2	40	168	*e*		

[a] In the presence of a catalytic amount of methanesulfonic acid. [b] Determined by weight after fractional recrystallisation. [c] In sealed flask. [d] Recovered 80% starting material. [e] Starting material recovered quantitatively; under drastic reaction conditions extensive polimerization occurs.



Scheme 2

(Z)-1,2,4-*Triphenylbut*-1-*en*-3-*yne* **4**.—A solution of phenylethynylmagnesium bromide was prepared by the exchange reaction between ethylmagnesium bromide (0.105 mol in 250 cm^3 of Et_2O) and phenylacetylene (10.7 g, 0.105 mol in 50 cm^3 of Et_2O). To this solution, stirred at reflux temperature, was added dropwise a solution of 2-phenylacetophenone **9** (8.0 g, 41 mmol) in Et_2O (50 cm^3) over 15 min. After 2 h under reflux, the reaction mixture was worked up following a standard procedure. Crude 1,2,4-triphenylbut-3-yn-2-ol, obtained as a viscous yellow oil, was subjected to the dehydration step without further purification. The crude material was mixed with finely powdered $KHSO_4$ (2.8 g, 20 mmol) and the mixture heated at 70 °C under reduced pressure (0.5 Torr) for 1.5 h. After cooling, the residue was purified by column chromatography on silica gel. Elution with light petroleum–benzene (9:1) afforded (*Z*)-**4** (7.3 g, 63.6%) as white crystals (from EtOH), m.p. 81 °C (Found: C, 94.15; H, 5.8. $C_{22}H_{16}$ requires C, 94.25; H, 5.75%); δ_H 6.70–8.00 (16 H, m, 1 vinylic and 15 Ph).

This isomer was assigned the *Z*-configuration by comparison with the *E*-isomer prepared in the stereoselective coupling reaction described below. Support for a *cis*-arrangement of the phenyl group in the 1-position and of the phenylethynyl moiety in the 2-position came from the successful cyclisation of (*Z*)-**4** to 1-benzylidene-2-phenyl-1*H*-indenes **7** (*vide infra*).

(E)-1,2,4-*Triphenylbut*-1-*en*-3-*yne* **4**. This compound was prepared by the same procedure described for the synthesis of the butenyne **3**, from copper(I) phenylacetylide (0.5 g, 3.03 mmol) and (*E*)-2-bromo-1,2-diphenylethene **10** (0.56 g, 2.16 mmol) in dry pyridine (11 cm^3) under reflux for 12 h. Crude (*E*)-**4** (0.54 g, 88%) was isolated by column chromatography with light petroleum–benzene (9:1) as eluent. White crystals (from EtOH), m.p. 49–50 °C (Found: C, 94.25; H, 5.95. $C_{22}H_{16}$ requires C, 94.25; H, 5.75%); δ_H 6.90 (1 H, s, vinylic) and 7.00–7.80 (15 H, m, Ph).

(E)- *and* (Z)-1,4-*Diphenylbut*-1-*en*-3-*ynes* **12**.—The two isomers were prepared by treatment of copper(I) phenylacetylide (3.4 g, 20.8 mmol) with mixtures in various ratios of (*E*)- and (*Z*)-2-bromostyrenes **13** (3.8 g, 20.8 mmol) in boiling pyridine (80 cm^3) for 21 h, following the procedure described above. The isomeric compounds **12** (total yield 3.6 g, 85%) were, in all cases, formed in the same ratio as the starting mixtures of 2-bromostyrenes, and were separated by column chromatography. Elution with light petroleum afforded first (*E*)-**12** and then (*Z*)-**12**. The column chromatography was carried out as quickly as possible to avoid isomerisation of the *Z*-isomer on prolonged contact with silica gel.

(*E*)-1,4-Diphenylbut-1-en-3-yne **12** was further purified by recrystallisation and obtained as white crystals (from EtOH), m.p. 96–97 °C (lit.,[25] m.p. 96.5–97 °C). (*Z*)-1,4-Diphenylbut-1-en-3-yne **12**, a pale yellow oil,[15] was purified by bulb-to-bulb distillation under reduced pressure (1×10^{-3} Torr, bath temperature 145 °C) (Found: C, 94.15; H, 5.85. $C_{16}H_{12}$ requires C, 94.12; H, 5.88%); ν_{max}(liquid film)/cm^{-1} 2190w (C≡C); δ_H 5.80 (1 H, d, *J* 11.5, vinylic), 6.55 (1 H, d, *J* 11.5, vinylic) and 7.00–8.10 (10 H, m, Ph). This compound must be stored in the refrigerator and in the dark to avoid *cis–trans* isomerisation.

Cyclisation of Butenynes to Methylene-1H-*indenes: General Procedure*.—To a solution of the appropriate butenyne (3.5 mmol) in anhydrous dichloromethane or 1,2-dibromoethane (60 cm^3) methanesulfonic acid (1 mmol) was added and the mixture was heated and maintained at reflux until no more starting material could be detected by TLC. After cooling, the solution was filtered through a 20 mm thick layer of dry silica gel, and the solvent was evaporated under reduced pressure. The residue was then column chromatographed with light petroleum–benzene (10:1) as eluent.

1-*Benzylidene*-2,3-*diphenyl*-1H-*indene* **5**.—Yellow crystals (from EtOH), purified by recrystallisation from ethanol, m.p. 185–186 °C (lit.,[26] m.p. 185 °C).

(E)- *and* (Z)-1-*Benzylidene*-3-*phenyl*-1H-*indenes* **6**.—Fractional recrystallisation from MeOH of the mixture obtained by column chromatography afforded (*E*)-**6** as a yellow–orange solid, m.p. 77 °C (lit.,[17] 77.5 °C); ν_{max}(KBr)/cm^{-1} 1347 (exocyclic C=C); λ_{max}/nm (log ε) 243 (4.43), 252 (4.44), 296 (4.25) and 352 (4.39); δ_H 6.96 (1 H, s, vinylic) and 7.10–7.70 (15 H, m, Ph). Isomer (*Z*)-**6** was similarly obtained as a yellow solid, m.p. 145–146 °C (Found: C, 94.35; H, 5.65. $C_{22}H_{16}$ requires C, 94.25; H, 5.75%); ν_{max}(KBr)/cm^{-1} 1340 (exocyclic C=C); λ_{max}/nm (log ε) 236 (4.35), 249sh (*ca.* 4.30) 291 (4.26) and 333 (4.15); δ_H 6.65 (1 H, s, vinylic) and 6.90–7.75 (15 H, m, Ph).

(E)- *and* (Z)-1-*Benzylidene*-2-*phenyl*-1H-*indenes* **7**.—Fractional recrystallisation from hexane permitted us to isolate (*E*)-**7** as a yellow solid, m.p. 130–131 °C (lit.,[12] 129–131 °C); δ_H

6.85–7.30 (14 H, m, 1 vinylic and 13 Ph) and 7.55–7.80 (2 H, m, Ph). Evaporation of the mother liquor afforded (*Z*)-**7** as an orange oil, which was purified by bulb-to-bulb distillation under reduced pressure (1×10^{-3} Torr, bath temperature 150 °C) (lit.,[12] b.p. 160 °C at 0.06 Torr); δ_H 6.82 (1 H, s, vinylic) and 6.90–7.70 (15 H, m, Ph).

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