# Double Ring Closure of Diacetylenic Compounds with Activated Olefins in the Presence of a Cobalt(0) Catalyst

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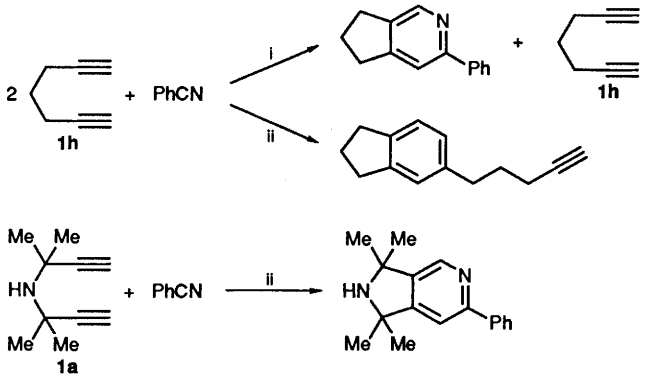
Ring formation from 1,6- or 1,7-diynes and activated olefins is catalysed by cobalt(0) complexes through cobaltacyclopentadiene intermediates. If steric hindrance is sufficiently low the reaction proceeds further and products containing two molecules of olefin per molecule of diyne are obtained. With terminally alkyl-substituted and conformationally rigid diynes the reaction must be carried out stoichiometrically because of the incursion of a new acid/base-catalysed reaction, which is independent of cobalt.

Cobalt(I) catalysis of alkyne cyclotrimerization or of alkyne–nitrile cyclocotrimerization [1] has attracted the interest of several research groups.

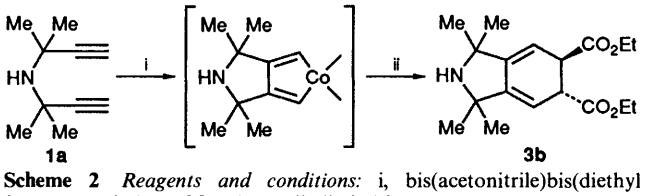
In the course of our studies on cobalt-catalysed reactions of diynes with unsaturated substrates we reported on the striking difference in behaviour of cobalt(0) and cobalt(I) complexes.[2] Although both favour the formation of metallacycles from 1,6- or 1,7-diynes, the former catalyses the incorporation of alkynes rather than nitriles into the metallacycle, while the latter prefers nitriles to alkynes. For example, hepta-1,6-diyne prefers the acetylenic triple bond in the presence of cobalt(0), but reacts with nitriles in the presence of a cobalt(I) catalyst (Scheme 1).



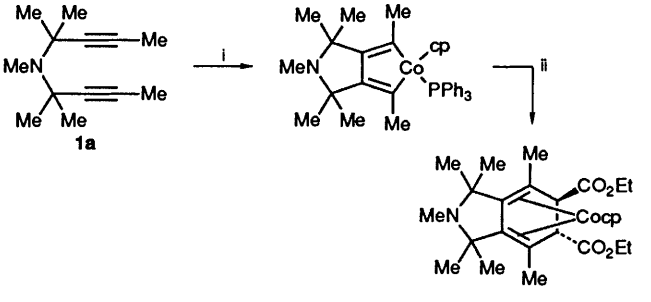

**Scheme 1** *Reagents and conditions:* i, $cpCo(CO)_2$, 80 °C, toluene; ii, bis(acetonitrile)bis(diethyl fumarate)cobalt, 80 °C, toluene

Cobalt(0), however, becomes a very efficient catalyst for incorporation of nitrile when geminal groups *alpha* to the triple bonds or other groups, able to exert conformational and steric effects on formation and reactivity of the intermediate metallacycle, are present; for example, tetramethyldipropargylamine [bis(1,1-dimethylprop-2-ynyl)amine] (Scheme 1) reacts with benzonitrile to give a condensed pyridine in high yield.[2]

Another instance of different reactivity of cobalt(0) and cobalt(I) complexes was observed in the reaction of diynes with activated olefins. As briefly reported recently,[3] cobalt(0) gives cyclic products deriving from incorporation of olefin into a cobaltacyclopentadiene intermediate (see, for example, Scheme 2), while cobalt(I) cyclopentadienyl complexes are reluctant to react in the presence of the co-ordinating ligands usually present, and require higher temperatures and longer times to give new cobalt complexes. The latter contain as ligand the cyclic product derived from incorporation of olefin and are very stable.[4] Thus the complex obtained from cyclopentadienylbis(triphenylphosphine)cobalt and heptamethyldipropargylamine [bis(1,1-dimethylbut-2-ynyl)methylamine] (Scheme 3) does not react until a sufficiently high temperature is attained to replace triphenylphosphine.[5] The reaction then occurs, but the organic product is not released significantly from the complex.




**Scheme 2** *Reagents and conditions:* i, bis(acetonitrile)bis(diethyl fumarate)cobalt, 80 °C, toluene; ii, diethyl fumarate




**Scheme 3** *Reagents and conditions:* i, cyclopentadienylbis(triphenylphosphine)cobalt, 80 °C, toluene; ii, diethyl fumarate

A rather unstable cobalt(I) complex, (butadiene)-5-methylhepta-2,6-dienylcobalt, does catalyse the reaction of the diacetylenic ligand with the activated olefins, however, although with modest yield and selectivity.[3]

These facts, as well as the isolation and reactivity of cobaltacyclopentadiene complexes, led us to interpret the results as the consequence of the different accessibility of the olefin to the metal centre and of the different stability of the complexes, resulting from the reaction of diynes with olefins.[5]

Cobalt(0) complexes allow a better accessibility of the olefin to the metal centre as well as lowering the stability of the complex which co-ordinates the reaction product of the diyne with the olefin.

In view of the ability of cobalt(0) to catalyse the reaction of diynes with activated olefins we explored the synthetic potential of the new method, and the results are reported in the present paper.

Another interesting aspect emerged from our efforts to extend the scope of our reaction. When alkyl substituents were present on the terminal acetylenic carbons of certain substrates another reaction, not involving cobalt, was superimposed on the

**Table 1** Reactions of diynes **1** and **11** with olefins **2**, 1:15 molar ratio [except for entries 12–18 and 21 (1:3)] in the presence of cobalt complexes in toluene (0.1 mol $dm^{-3}$)

| Entry | Diyne | Olefin | Cobalt catalyst[a] | Diyne/Co molar quotient | $T$/°C | $t$/h | Conversion (%)[b] | Yield[b] 3 | | 4 | 5 | 6 | 7 | Other products (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **1a** | **2a** | A | 5 | 0 | 0.5 | 97 | **a** 86 | (75) | | | | | |
| 2 | **1a** | **2a** | A | 10 | 60 | 0.5 | 100 | **a** 87 | (75) | | **a** 3 | | | |
| 3 | **1a** | **2b** | A | 5 | −6 | 0.5 | 100 | **b** 71,[c] 5,[d] 2[d] | | 6 | | **a** 12 | | |
| 4 | **1a** | **2b** | A | 15 | 80 | 24 | 100 | **b** 42,[c] 6[d] | | 27 | **b** 9 | **a** 12 | | |
| 5 | **1a** | **2c** | A | 10 | 80 | 24 | 65 | **b** 8,[c] 3,[d] 2[d] | | 13 | **b** 2 | **a** 24 | | |
| 6 | **1a** | **2d** | A | 5 | 80 | 5 | 85 | **c** 42 | (34) | | | **a** 34 | | |
| 7 | **1a** | **2e** | A | 5 | 80 | 5 | 85 | **d** 47 | (38) | | | **a** 32 | | |
| 8 | **1a** | **2f** | B | 10 | 80 | 7 | 86 | **e** 22,[e] 11[d] | | | | **a** 16 | | |
| 9 | **1a** | **2g** | B | 10 | 65 | 6 | 96 | **f** 36,[f] 3,[d] 3,[d] 1[d] | | | | **a** 9 | | |
| 10 | **1b** | **2a** | A | 10 | 25 | 0.5 | 100 | **g** >98 | (90) | | | | | |
| 11 | **1b** | **2b** | C | 10 | 80 | 4 | 98 | **h** 68,[g] 7,[d] 7,[d] 3[d] | | | **e** 7 | | | |
| 12 | **1c** | **2b** | A | 1 | 60 | 7 | 100 | **i** >98 | (90) | | | | | |
| 13 | **1d** | **2b** | A | 1 | 60 | 7 | 98 | **j** 89 | (80) | | | | | |
| 14 | **1c** | **2b** | A | 10 | 60 | 7 | 92 | **i** 35 | | | | | | **8b** 42 |
| 15 | **1c** | **2a** | A | 10 | 60 | 4 | 82 | **k** 33 | (25) | | | | | **8a** 36 |
| 16 | **1c** | **2c** | A | 1 | 60 | 7 | 68 | **i** 32 | | | | | | **8c** 28 |
| 17 | **1e** | **2b** | A | 5 | 100 | 20 | 82 | **l** 55 | (47) | | | | | |
| 18 | **1e** | **2c** | B | 5 | 100 | 8 | 75 | | | | | | | **9** 49 |
| 19 | **1b** | **2h** | A | 1 | 80 | 8 | 89 | | | | **f** (75) | | | |
| 20 | **1f** | **2h** | A | 1 | 80 | 8 | 75 | | | | **g** (59) | | | |
| 21 | **1c** | **2h** | A | 1 | 80 | 8 | 64 | | | | **h** (42) | | | |
| 22 | **1g** | **2a** | B | 10 | 80 | 24 | 77 | | | | | | **a** (18)[h] | |
| 23 | **1b** | **2a** | B | 10 | 80 | 24 | 87 | | | | | | **b** (30)[i] | |
| 24 | **1h** | **2a** | B | 10 | 80 | 20 | 98 | | | | | | **c** (45)[j] | |
| 25 | **1i** | **2b** | A | 10 | 60 | 3 | 95 | **m** 84 | (77) | | | | | |
| 26 | **1j** | **2b** | A | 10 | 60 | 16 | 65 | **n** 43 | (37) | | | **b** (15) | | **12** 68[k] |
| 27 | **1l** | **2a** | A | 10 | 45 | 12 | 90 | | | | | | | |

[a] Cobalt catalysts; A = $\{(MeCN)_2[(E)\text{-}EtO_2CCH{=}CHCO_2Et]_2Co\}$; B = $Co_2(CO)_8$; C = complex **10**. [b] Based on substrate **1**, determined by GLC; yield of isolated products are in parentheses. [c] In entries 3–5 product **3b** and its isomers were isolated as isomer **4** in 70, 65 and 20% yield, respectively, including pre-existing compound **4**. [d] GLC yields of unidentified isomers of products **3** from double-bond shift. [e] Product **3e** and its isomers were isolated after aromatization to compound **5c** (23% yield). [f] Product **3f** and its isomers were isolated after aromatization to compound **5d** (33% yield). [g] Product **3h** and its isomers were isolated after aromatization to compound **5e** (64% yield, including pre-existing **5e**). [h] Four isomers, 62% yield (22:15:27:36 GLC proportions); only the most abundant one could be separated, 18% yield. [i] Two major isomers, 52% yield (4:1 GLC ratio); the most abundant one, *cis*, was isolated, 30% yield. [j] Three major isomers, 96% yield (52:31:17 GLC proportions); the most abundant one, *cis*, was isolated, 45% yield. [k] Product **12** (two isomers) was isolated after aromatization to compound **13** (55% yield).

expected cobalt-controlled one. The new reaction occurred in the absence of cobalt and led to exocyclic methylenecyclohexene compounds. The scope and mechanism of this reaction, briefly reported previously,[3] will be described in the following paper.

## Results

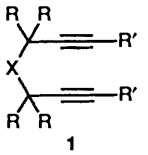
Table 1 reports the results of the reaction of diynes **1** with olefins **2** in the presence of cobalt(0) catalysts, as illustrated in the example of Scheme 2. Compounds **3**–**13** are referred to in Table 1. Bis(acetonitrile)bis(diethyl fumarate)cobalt(0)[6] was extensively used throughout the study reported here, as it was the most effective catalyst in general. It required, however, careful elimination of oxygen from the reaction mixture. Up to 15 mol of diyne per mol of catalyst were used, but no optimization work was carried out.

In some cases better selectivity could be obtained with $Co_2(CO)_8$ or with complex **10**, a dimeric complex isolated from a $Co_2(CO)_8$-catalysed reaction.[7] The $CoCl_2$/Mn system, previously used by us for the synthesis of the pyridine ring,[2] was found to be ineffective for diyne–olefin reactions, probably because of competition for co-ordination between chloride ions and the olefin.

Since the simplest 1,6-diynes, containing methylene groups adjacent to the triple bonds, gave the most complex reaction mixtures, including the addition product of two molecules of activated olefin to the diyne, some substituted diynes, which cleanly reacted with one molecule of olefin, are considered first.

Substrates of this kind contain geminal groups on the carbon atoms near to the triple bond. As previously observed[2] this circumstance favours a suitable conformation for formation of a cobaltacycle and it also prevents addition of further olefin to the first formed product at low (near to room) temperature. Dipropargylamines are readily accessible substrates which react with activated olefins in good yield. An excess of olefin (~15 mol per mol of diyne) is necessary to ensure successful competition with the acetylenic substrates, which otherwise would give a dimer such as **6**. This large excess is no longer needed with all-substituted diacetylenic compounds **1c–e**. A small amount of toluene is added to adjust cobalt concentration to ~0.1 mol $dm^{-3}$. Suitable temperatures for these reactions range from −10 to 100 °C. The lower limit refers to substrates with R′ = H, while bulkier R′ substituents require higher temperatures. Thus dipropargylamine with R = Me, R′ = H (**1a**) reacted with ethyl acrylate **2a** at 0 °C (entry 1) to give product **3a** in 86% yield. At 60 °C a small amount of the corresponding aromatic compound **5a** was also formed (entry 2). Compound **3b** was obtained in 71% yield from reaction with diethyl fumarate **2b** at −6 °C; two other, unidentified isomers (2 and 5%, respectively, from double-bond shift, see later), together with isomer **4** (6%) and compound **6a** (dimerization product of the diyne) (12%) were also present (entry 3).

It is noteworthy that the fumarate carboxy groups retain their stereochemistry. This cannot be seen from $^1H$ NMR coupling constants because of the proton magnetic equivalence,



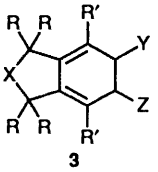
1

| 1 | X | R | R′ |
|---|---|---|---|
| a | NH | Me | H |
| b | NMe | Me | H |
| c | NMe | Me | Me |
| d | NMe | Me | Et |
| e | NMe | Me | $SiMe_3$ |
| f | NMe | Me | H, Me |
| g | $NCO_2Me$ | H | H |
| h | $CH_2$ | H | H |
| i | $CH_2$ | H | Me |
| j | $CH_2CH_2$ | H | Me |

Y–CH=CH–Z

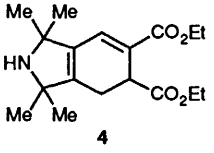
2

| 2 | Y | Z |
|---|---|---|
| a | H | $CO_2Et$ |
| b | (*E*) $CO_2Et$ | $CO_2Et$ |
| c | (*Z*) $CO_2Et$ | $CO_2Et$ |
| d | (*E*) Ph | $CO_2Et$ |
| e | (*E*) Me | $CO_2Et$ |
| f | H | Ph |
| g | H | CN |
| h | OCN(Ph)CO | |



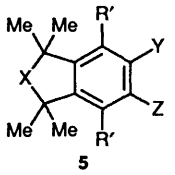
3

| 3 | X | R | R′ | Y | Z |
|---|---|---|---|---|---|
| a | NH | Me | H | H | $CO_2Et$ |
| b | NH | Me | H | $CO_2Et$ | $CO_2Et$ |
| c | NH | Me | H | Ph | $CO_2Et$ |
| d | NH | Me | H | Me | $CO_2Me$ |
| e | NH | Me | H | H | Ph |
| f | NH | Me | H | H | CN |
| g | NMe | Me | H | H | $CO_2Et$ |
| h | NMe | Me | H | $CO_2Et$ | $CO_2Et$ |
| i | NMe | Me | Me | $CO_2Et$ | $CO_2Et$ |
| j | NMe | Me | Et | $CO_2Et$ | $CO_2Et$ |
| k | NMe | Me | Me | H | $CO_2Et$ |
| l | NMe | Me | $SiMe_3$ | $CO_2Et$ | $CO_2Et$ |
| m | $CH_2$ | H | Me | $CO_2Et$ | $CO_2Et$ |
| n | $CH_2CH_2$ | H | Me | $CO_2Et$ | $CO_2Et$ |



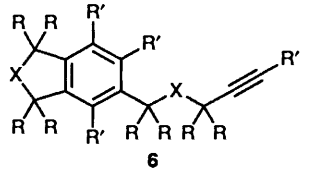
4

but it is readily observed with other products such as **3c** and **3d**, derived from other *E* esters **2d** and **2e** (entries 6 and 7; see Experimental section). At higher temperatures, and for longer reaction times, the isomerization process proceeds further, leading to substantial amounts of compound **4** (entry 4). A similar isomerization readily occurs on handling products, particularly those derived from fumarate, on silica. For this reason some products **3** have been isolated and characterized



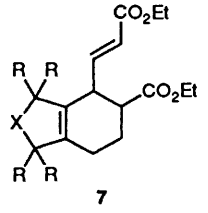
5

| 5 | X | R′ | Y | Z |
|---|---|---|---|---|
| a | NH | H | H | $CO_2Et$ |
| b | NH | H | $CO_2Et$ | $CO_2Et$ |
| c | NH | H | H | Ph |
| d | NH | H | H | CN |
| e | NMe | H | $CO_2Et$ | $CO_2Et$ |
| f | NMe | H | OCN(Ph)CO | |
| g | NMe | H, Me | OCN(Ph)CO | |
| h | NMe | Me | OCN(Ph)CO | |



6

| 6 | X | R | R′ |
|---|---|---|---|
| a | NH | Me | H |
| b | $CH_2CH_2$ | H | Me |



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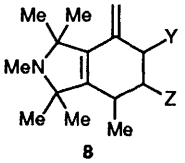
| 7 | X | R |
|---|---|---|
| a | $NCO_2Me$ | H |
| b | NMe | Me |
| c | $CH_2$ | H |

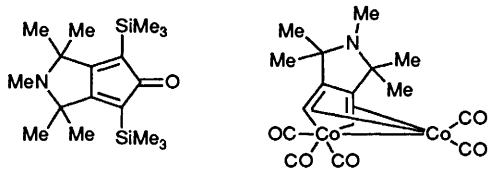


8

| 8 | Y | Z |
|---|---|---|
| a | H | $CO_2Et$ |
| b | $CO_2Et$ | $CO_2Et$ (*trans*)[a] |
| c | $CO_2Et$ | $CO_2Et$ (*cis*)[a] |

[a] In respect to Y; two isomers (cis or *trans*) in respect to Me.

as their more stable isomer **4** (entries 3–5). Product **3b** (and analogously other products **3** in general) could be recognized in its mixtures with other isomers because of its characteristic $^1H$ NMR absorptions centred at $\delta$ 3.4 ($CHCO_2R$) and 5.6 (–CH=). Surprisingly, with diethyl maleate **2c** as the activated



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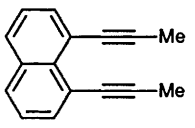
10



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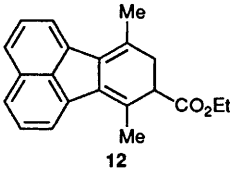

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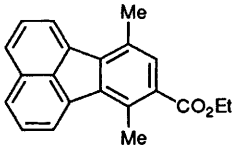


13

olefin, the yield fell sharply (26% overall yield of reaction products with **2c**) and the same product **3b** as obtained from diethyl fumarate was formed, together with isomer **4** and other isomers, the diyne dimer **6a** and polymerization products (entry 5). Conversion was low, even after 24 h at 80 °C. The yield also decreased when disubstituted olefins with only one electron-withdrawing substituent were used. Diyne dimers were formed to a large extent (entries 6 and 7).

An olefin singly substituted by an aryl group (styrene **2c**) was also used [entry 8, $Co_2(CO)_8$ as catalyst]. The isomeric product mixture, containing **3e** predominantly, as seen from NMR signals, was converted into the aromatic compound **5c**. Dimer **6a** was also present.[2a] A similar reaction with acrylonitrile **2g** led to the selective incorporation of the double bond and not of the cyano group, the latter reaction being typical of cobalt(I).[1] The isomeric mixture was also converted into the corresponding aromatic compound, **5d** (entry 9), by Pd/C-catalysed aromatization at 140 °C.

Compared with **1a**, tertiary amine **1b** appears to give even better results. Thus, the reaction of substrate **1b** with ethyl acrylate **2a** at 25 °C afforded a product in a yield >98% (entry 10). Catalyst **10** also proved to be active: diethyl fumarate **2b** reacted at 80 °C with the same substrate **1b** to give a 68% yield of compound **3h**, along with 17% of three isomers (7:7:3, GLC peak areas) and 7% of the aromatized product **5** (entry 11). Compound **3h** and its isomers were converted into compound **5e** by aromatization as above.

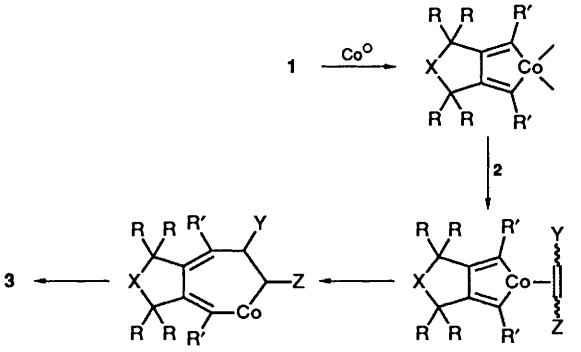
Diethyl fumarate **2b** at 60 °C also gave a yield >98% with the all-methylated compound **1c** (entry 12) and an 89% yield with substrate **1d** (entry 13). In these cases, however, care must be taken not to use more than 1:1 dialkyne:cobalt catalyst molar ratio because of the incursion of the uncatalysed reaction leading to compounds **8** (entry 14), to be discussed in the following paper. Similar behaviour was observed also for ethyl acrylate **2a** (entry 15). In the case of diethyl maleate **2c** (entry 16) even a 1:1 substrate:catalyst ratio did not prevent the uncatalysed reaction. Product **3i** is the same as that obtained from the fumarate **2b**. Bulky substituents such as $SiMe_3$ on the terminal carbon of the triple bond (substrate **1e**) allowed the reaction with diethyl fumarate **2b** to occur, although it proceeded in lower yield (compound **3l**, entry 17), but diethyl maleate **2c** did not react. If $Co_2(CO)_8$ was used as catalyst for the same reaction, insertion of CO occurred to give compound **9** (entry 18). It is noteworthy that *Z* compounds do not always behave as poorly as did diethyl maleate **2c** in their reactions with diynes. With dipropargylamines **1b**, **1f** and **1c**, *N*-phenylmaleimide **2h** gave 75, 59, and 42% yields of the aromatic compounds **5f**, **5g** and **5h**, resulting from dehydrogenation of the corresponding products **3** (entries 19–21) and possibly to some extent from dehydrogenation of **8**-type products from the uncatalysed reaction (see following paper).

Substrates with R′ = H undergo more complex reactions at 80 °C or above if monosubstituted olefins such as ethyl acrylate **2a** are used. Products are formed which derive from the addition of two molecules of acrylate, one forming the cyclohexene ring and the other one an *E*-acrylic chain (**7a–c**) (entries 22–24). The best selectivities were obtained when using $Co_2(CO)_8$ as catalyst. *cis,trans* and *Z,E* Isomers and minor amounts of other isomers from double-bond shift gave rise to very tightly packed series of GLC peaks. The major isomers of products **7b** and **7c** could be isolated, however, and their $^1H$ NMR signals were consistent with *E,cis* stereochemistry. The major isomer of product **7a** (*E*) did not allow a clear assignment, but is likely to be *cis* by analogy with the corresponding products **7b** and **7c**. It is worth noting that it is sufficient that two methyl groups are present on the terminal acetylenic carbons (**1i**) to obtain compound **3m** in 84% yield (entry 25), corresponding to the addition of one molecule of ethyl acrylate **2a** to one molecule of nonadiyne **1i**. The use of a longer chain as in deca-2,8-diyne **1j** (entry 26) led to a lower yield of the corresponding product **3n**, dimerization of the starting diyne to product **6b** taking place to a substantial extent. The same substrate gave low yields (not determined quantitatively) in the reaction with styrene **2f** and with acrylonitrile **2g**.

Substrate **11** was tested in order to ascertain whether rigidly held, parallel alkynyl groups could be caused to react as well. The reaction (entry 27) with ethyl acrylate **2a** gave compound **12** in 68% yield at 90% conversion. The product showed a strong tendency to isomerize by double-bond shift and was identified as compound **13** after aromatization on Pd/C at 140 °C.

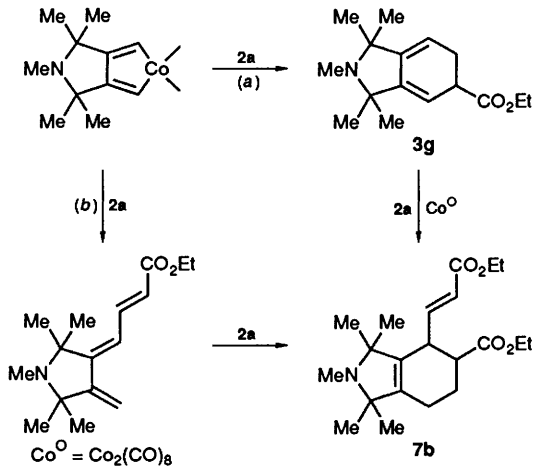
## Discussion

There is little doubt that the mechanism of the cobalt(0)-catalysed reaction of diynes with olefins involves formation of a metallacycle. Similar 2 + 2 + 2 reactions have been described recently when rhodium(I) was used as catalyst and their mechanism has been interpreted analogously.[8] In our case the isolation of complex **10** and its reactivity with activated double bonds to give the corresponding products **3** [5] is in agreement with the catalytic cycle depicted in Scheme 4.



Scheme 4

The intermediate metallacycle may be present in the form of a dimer analogous to **10**, containing olefinic ligands and possibly acting as a source of a reactive monomeric form. Scheme 4 reports olefinic co-ordination and ring enlargement as the subsequent steps. At present an alternative pathway, consisting of the direct attack of the olefin on the cobalta-cyclopentadiene in a sort of Diels–Alder reaction[9] cannot be excluded, however.




Scheme 5

The addition of a second molecule of activated olefin may proceed in two routes as exemplified in Scheme 5. Route *a* involves further Co-catalysed addition to compound **3g**. This reaction has been carried out separately with $Co_2(CO)_8$ as catalyst, and compound **7b** was obtained in 23% yield. Route *b* finds support in the literature, which reports Co-catalysed reaction of dienes with activated olefins,[10] in the regiochemistry of the reaction, and in the predominantly *cis* structure of the product with substrate **2a**, which are in agreement with a Diels–Alder-type reaction,[11] so at present we are not able to specify whether both pathways are at work or if a preferred pathway is followed.

Cobalt(0)-catalysed reactions are stereospecific insofar as the stereochemistry of the starting olefin is retained. When *Z*-to-*E* isomerization is easier than *Z* olefin incorporation, however, as in the case of diethyl maleate **2c**, only the product corresponding to the reaction of the *E*-isomer is obtained. Incorporation of a *Z*-olefin of the type of *N*-phenylmaleimide leads to a strained, flattened ring which readily aromatizes by dehydrogenation.

The presence of another asymmetric centre as in the case of compounds with R′ = Me gives rise to two (*cis* and *trans*) stereoisomers.

In conclusion, a new synthetic method for preparing condensed cyclohexadienes from 1,6- or 1,7-diynes and activated olefins has been worked out, based on the catalytic action of cobalt(0) complexes.

## Experimental

Bis(acetonitrile)bis(diethyl fumarate)cobalt[6] and complex **10**[7] were prepared according to the literature.

All the starting olefinic materials **2a–h** were pure commercial products (Fluka, Strem, Aldrich). The substrates, tetramethyldipropargylamine **1a**,[12] *N*-substituted dipropargylamines **1b** and **1h**[13] and product **11**[14] were synthesized according to reported procedures. Alkylation and silylation of terminal acetylene groups were also carried out according to preparations reported in the literature.[5,15]

Product mixtures were analysed by TLC or by GLC with a methylsilicone (OV101 stationary phase) capillary column at an initial temperature of 60 °C with a gradient of 20 °C $min^{-1}$ to the final hold temperature of 280 °C. Quantitative determination of the products and of the starting substrates, if not otherwise specified, was carried out by GLC by using the internal standard method. Isolation of products was performed by flash chromatography or preparative TLC (PLC) on silica gel or alumina with a suitable eluent. Merck silica gel 60 (230–400 mesh) was used for column chromatography. Analytical TLC plates and silica gel 60 F254 for PLC were purchased from Merck. Solvents were purified, dried by standard methods, and stored over molecular sieves (Type 4 Å 1/8 pellets, Union Carbide).

M.p.s and b.p.s were determined using a Büchi 530 apparatus and are uncorrected. B.p.s refer to the bath temperature. Elemental analyses were carried out with a Carlo Erba Mod. 1106 elemental analyser. IR spectra were recorded on a Perkin-Elmer 298 spectrometer. Mass spectra were obtained using a Finnigan 1020 spectrometer at 70 eV ionizing voltage. $^1H$ and $^{13}C$ NMR spectra were taken on AC100, CXP200 or AMX400 Bruker spectrometers and are reported in $\delta$-units with $Me_4Si$ as internal standard; *J*-values are given in Hz.

*Reaction of Diynes* **1** *with Olefins* **2** *in the Presence of Cobalt Complexes.*—In a typical experiment bis(acetonitrile)bis(diethyl fumarate)cobalt (0.078 g, 0.16 mmol), diyne **1a** (0.12 g, 0.8 mmol), ethyl acylate **2a** (1.25 g, 12.5 mmol) and some toluene, to adjust the concentration of Co to 0.1 mol $dm^{-3}$, were placed at 0 °C under $N_2$ in a flask equipped with a side-arm and a magnetic bar. The stirred reaction mixture was kept at 60 °C for 30 min. After filtration through Celite to eliminate the metal, conversion of substrate **1a** (100%) and yields were determined by GLC. The yield of product **3a** (172 mg, 0.69 mmol) was 87% and that of product **5a** (6 mg, 0.025 mmol) was 3%. Products **3a** and **5a** were isolated by TLC on silica gel (hexane–acetone 70:30), after distillation of ethyl acrylate at low pressure.

*Reaction of Diynes* **1b**, **1g** *and* **1h** *with Olefin* **2a** *in the Presence of Dicobalt Octacarbonyl.*—In a typical experiment $Co_2(CO)_8$ (0.068 g, 0.2 mmol), hepta-1,6-diyne **1h** (0.185 g, 2.0 mmol) and ethyl acrylate **2a** (3.0 g, 30 mmol) were allowed to react at 80 °C for 20 h. After filtration through Celite, conversion of substrate **1h** (96%) was determined by GLC. Three isomers of the corresponding product **7** (52, 31, 17% selectivity) were present in the mixture; only compound **7c** (0.263 g, 45% yield based on **1h**) was isolated as a pure product by column chromatography on neutral $Al_2O_3$ (hexane–ethyl acetate 70:30).

*Properties of New Substrates and Products.*—Bis-(1,1-dimethylprop-2-ynyl)methylamine **1d**, oil, b.p. 100 °C (150 Pa); $\delta_H$(100 MHz; $CDCl_3$) 0.95 (6 H, t, *J* 7.1, 2 × Me), 1.52 (12 H, s, 4 × Me), 2.13 (4 H, q, *J* 7.1, 2 × $CH_2$) and 2.31 (3 H, s, NMe); *m/z* 219 ($M^+$), 205 (15), 204 (100), 174 (30), 160 (28) and 56 (51).

Bis-(1,1-dimethyl-3-trimethylsilylprop-2-ynyl)methylamine **1e**, oil, b.p. 117 °C (150 Pa); $\delta_H$(100 MHz; $CDCl_3$) 0.25 (18 H, s, 6 × Me), 1.48 (12 H, s, 4 × Me) and 2.33 (3 H, s, NMe); *m/z* 307 ($M^+$), 293 (33), 292 (50), 155 (74), 154 (100), 97 (52), 73 (26), 56 (21) and 49 (23).

*N*-(1,1-Dimethylprop-2-ynyl)-*N*-methyl-1,1-dimethylbut-2-ynylamine **1f**, oil, b.p. 69 °C (150 Pa); $\delta_H$(100 MHz; $CDCl_3$) 1.53 (12 H, br s, 4 × Me), 1.77 (3 H, s, Me), 2.30 (1 H, s, ≡CH) and 2.33 (3 H, s, NMe); *m/z* 177 ($M^+$), 163 (100), 162 (73), 147 (34), 146 (35), 132 (20), 72 (20) and 56 (42).

*Ethyl* 1,1,3,3-*tetramethyl*-2,3,5,6-*tetrahydro*-1H-*isoindole*-5-*carboxylate* **3a**. Isolated by PLC on silica gel (hexane–acetone 70:30). Pale yellow oil, b.p. 94 °C (8 Pa) (Found: C, 72.2; H, 9.2; N, 5.6. $C_{15}H_{23}NO_2$ requires C, 72.29; H, 9.24; N, 5.62%); $\nu_{max}$(film)/$cm^{-1}$ 3320, 2960, 1735, 1360, 1270, 1160, 1085, 1030, 995 and 820; $\delta_H$(200 MHz; $CDCl_3$) 1.24 (6 H, s, 2 × Me), 1.26 (3 H, t, *J* 7.1, Me), 1.29 (6 H, s, 2 × Me), 1.78 (1 H, br s, NH), 2.38–2.56 (2 H, m, CHCO and C*H*H), 3.30 (1 H, ddd, *J* 11.8, 11.5, 3.2, CH*H*), 4.17 (2 H, q, *J* 7.1, $CH_2$), 5.42 (1 H, dd, *J* 4.6, 3.2, =CH) and 5.43 (1 H, d, *J* 3.8, =CH); *m/z* 249 ($M^+$ absent), 235 (13), 234 (100), 145 (13) and 144 (16).

*Methyl* 1,1,3,3-*tetramethyl*-6-*phenyl*-2,3,5α,6β-*tetrahydro*-1H-*isoindole*-5-*carboxylate* **3c**. Isolated by PLC on silica gel

(hexane–acetone 90:10). Pale yellow oil, b.p. 152 °C (15 Pa) (Found: C, 77.1; H, 8.05; N, 4.4. $C_{20}H_{25}NO_2$ requires C, 77.17; H, 8.04; N, 4.50%); $\nu_{max}$(film)/cm$^{-1}$ 3330, 2960, 1735, 1600, 1480, 1360, 1270, 890, 820, 770 and 700; $\delta_H$(200 MHz; $CDCl_3$) 1.30, 1.31 and 1.34 (12 H, 3 s, 4 × Me), 1.80 (1 H, br s, NH), 3.45 (1 H, dd, *J* 10.8, 4.0, CH), 3.66 (3 H, s, OMe), 4.15 (1 H, dd, *J* 10.8, 3.8, CH), 5.29 and 5.40 (2 H, 2 d, *J* 4.0, 3.8, 2 × =CH) and 7.12–7.29 (5 H, m, Ph); *m/z* 311 ($M^+$ absent), 297 (14), 296 (100), 295 (28) and 236 (18).

*Methyl* 1,1,3,3,6-*pentamethyl*-2,3,5α,6β-*tetrahydro*-1H-*isoindole*-5-*carboxylate* **3d**. Isolated by PLC on silica gel (hexane–acetone 40:60). Pale yellow oil, b.p. 110 °C (8 Pa) (Found: C, 72.1; H, 9.2; N, 5.6. $C_{15}H_{23}NO_2$ requires C, 72.29; H, 9.24; N, 5.62%); $\nu_{max}$(film)/cm$^{-1}$ 3320, 2960, 1735, 1435, 1360, 1270, 1160, 1090, 1030, 1000 and 820; $\delta_H$(200 MHz; $CDCl_3$) 1.07 (3 H, d, *J* 6.2, Me), 1.27 (12 H, br s, 4 × Me), 1.76 (1 H, br s, NH), 2.85–2.99 (1 H, m, CH), 2.97 (1 H, d, *J* 2.7, CHCO), 3.72 (3 H, s, OMe) and 5.26–5.30 (2 H, m, 2 × =CH); *m/z* 249 ($M^+$ absent), 235 (22), 234 (100), 233 (49), 174 (23), 160 (26) and 144 (14).

*Ethyl* 1,1,2,3,3-*pentamethyl*-2,3,5,6-*tetrahydro*-1H-*isoindole*-5-*carboxylate* **3g**. Isolated by PLC on silica gel (hexane–acetone 70:30). Oil, b.p. 106 °C (8 Pa); (Found: C, 72.9; H, 9.45; N, 5.3. $C_{16}H_{25}NO_2$ requires C, 73.00; H, 9.51; N, 5.32%); $\nu_{max}$(film)/cm$^{-1}$ 2960, 1735, 1360, 1270, 1160, 1080, 995 and 820; $\delta_H$(200 MHz; $CDCl_3$) 1.12, 1.13, 1.14 and 1.17 (12 H, 4 s, 4 × Me), 1.26 (3 H, t, *J* 7.1, Me), 2.26 (3 H, s, NMe), 2.38–2.58 (2 H, m, CH*H* and CHCO), 3.32 (1 H, ddd, *J* 13.5, 10.2 and 3.5, CH*H*), 4.16 (2 H, q, *J* 7.1, $CH_2$) and 5.38–5.47 (2 H, m, 2 × =CH); *m/z* 264 ($M^+$ + 1), 250 (19), 249 (100), 246 (63), 202 (21), 175 (26), 174 (56), 160 (27) and 56 (23).

*Diethyl* 1,1,2,3,3,4,7-*heptamethyl*-2,3,5aα,6β-*tetrahydro*-1H-*isoindole*-5,6-*dicarboxylate* **3i**. Isolated by PLC on silica gel (hexane–acetone 50:50). Oil, b.p. 145 °C (7 Pa) (Found: C, 69.35; H, 9.1; N, 3.85. $C_{21}H_{33}NO_4$ requires C, 69.42; H, 9.09; N, 3.86%); $\nu_{max}$(film)/cm$^{-1}$ 2980, 2860, 1740, 1470, 1230, 1100, 1035, 940 and 870; $\delta_H$(200 MHz; $CDCl_3$) 1.14 (6 H, s, 2 × Me), 1.18 (6 H, t, *J* 7.1, 2 × Me), 1.27 (6 H, s, 2 × Me), 1.97 (6 H, s, 2 × Me), 2.23 (3 H, s, NMe), 3.30 (2 H, s, 2 × CH) and 4.08 and 4.09 (4 H, q, *J* 7.1, 2 × $CH_2$); *m/z* 363 ($M^+$ absent), 362 ($M^+$ − 1), 348 (100), 274 (12) and 56 (18).

*Diethyl* 4,7-*diethyl*-1,1,2,3,3-*pentamethyl*-2,3,5α,6β-*tetrahydro*-1H-*isoindole*-5,6-*dicarboxylate* **3j**. Isolated by PLC on silica gel (hexane–acetone 65:35). Pale yellow oil, b.p. 160 °C (7 Pa) (Found: C, 70.5; H, 9.5; N, 3.5. $C_{23}H_{37}NO_4$ requires C, 70.59; H, 9.46; N, 3.58%); $\nu_{max}$(film)/cm$^{-1}$ 2980, 2880, 2820, 1735, 1470, 1370, 1230, 1100, 1035, 940 and 870; $\delta_H$(200 MHz; $CDCl_3$) 0.94 (6 H, t, *J* 7.5, 2 × Me), 1.10 (6 H, s, 2 × Me), 1.13 (6 H, t, *J* 7.1, 2 × Me), 1.26 (6 H, s, 2 × Me), 2.09 (2 H, dq, *J* 14.0, 7.5, 2 × C*H*H), 2.17 (3 H, s, NMe), 2.50 (2 H, dq, *J* 14.0, 7.5, 2 × CH*H*), 3.40 (2 H, s, 2 × CHCO) and 4.01 and 4.03 (4 H, q, *J* 7.1, 2 × $CH_2$); $\delta_C$(25 MHz; $CDCl_3$) 12.79 (2 × Me), 14.16 (2 × Me), 24.79 (Me), 25.12 (2 × $CH_2$), 25.30 (2 × Me), 25.34 (2 × Me), 45.77 (2 × CH), 60.57 (2 × $CH_2$), 61.74 (2 × qC), 124.45 (2 × qC), 141.04 (2 × qC) and 172.76 (2 × CO); *m/z* 391 ($M^+$), 378 (20), 377 (41), 376 (100), 302 (48), 230 (18), 215 (15) and 200 (15).

*Ethyl* 1,1,2,3,3,4,7-*heptamethyl*-2,3,5,6-*tetrahydro*-1H-*isoindole*-5-*carboxylate* **3k**. Isolated by PLC on silica gel (hexane–acetone 70:30). Oil, b.p. 129 °C (7 Pa) (Found: C, 74.2; H, 10.0; N, 4.8. $C_{18}H_{29}NO_2$ requires C, 74.23; H, 9.97; N, 4.81%); $\nu_{max}$(film)/cm$^{-1}$ 2980, 2940, 2900, 2880, 1735, 1460, 1370, 1260 and 1030; $\delta_H$(200 MHz; $CDCl_3$) 1.16 and 1.26 (12 H, 2 s, 4 × Me), 1.20 (3 H, t, *J* 7.2, Me), 1.84 and 1.92 (6 H, 2 s, 2 × Me), 2.27 (3 H, s, NMe), 2.28 and 2.41 (2 H, 2 d, *J* 7.3, 6.6, $CH_2$), 2.87 (1 H, dd, *J* 7.3, 6.6, CHCO) and 4.10 and 4.12 (2 H, 2 q, *J* 7.2, $CH_2$); *m/z* 291 ($M^+$), 277 (88), 276 (100), 275 (27), 248 (34), 202 (50), 188 (22), 187 (23), 186 (25) and 172 (28).

*Diethyl* 1,1,2,3,3-*pentamethyl*-4,7-*bis*(*trimethylsilyl*)-2,3,5α,-6β-*tetrahydro*-1H-*isoindole*-5,6-*dicarboxylate* **3l**. Isolated by PLC on silica gel (hexane–acetone 50:50). Pale yellow oil, b.p. 148 °C (7 Pa) (Found: C, 62.6; H, 9.4; N, 2.9. $C_{25}H_{45}NO_4Si_2$ requires C, 62.63; H, 9.39; N, 2.92%); $\nu_{max}$(film)/cm$^{-1}$ 2980, 1735, 1470, 1390, 1270, 1030 and 800; $\delta_H$(200 MHz; $CDCl_3$) 0.25 (18 H, s, 6 × Me), 1.07 (6 H, s, 2 × Me), 1.19 (6 H, t, *J* 7.1, 2 × Me), 1.38 (6 H, s, 2 × Me), 2.24 (3 H, s, NMe), 3.86 (2 H, s, 2 × CH) and 4.04 (4 H, q, *J* 7.1, 2 × $CH_2$); *m/z* 479 ($M^+$), 465 (100), 318 (18) and 73 (15).

*Diethyl* 4,7-*dimethyl*-2,3,5α,6β-*tetrahydroindene*-5,6-*dicarboxylate* **3m**. Isolated by PLC on silica gel (hexane–acetone 70:30). Oil, b.p. 124 °C (8 Pa) (Found: C, 69.8; H, 8.2. $C_{17}H_{24}O_4$ requires C, 69.86; H, 8.22%); $\nu_{max}$(film)/cm$^{-1}$ 2980, 2950, 1735, 1460, 1375, 1270, 1030 and 990; $\delta_H$(200 MHz; $CDCl_3$) 1.20 (6 H, t, *J* 7.3, 2 × Me), 1.69 (2 H, t, *J* 7.4, $CH_2$), 1.82 (6 H, s, 2 × Me), 2.23–2.38 (4 H, m, 2 × $CH_2$), 3.44 (2 H, s, 2 × CH) and 4.10 and 4.11 (4 H, 2 q, *J* 7.3, 2 × $CH_2$); *m/z* 292 ($M^+$), 246 (19), 219 (49), 218 (23), 173 (100), 147 (89), 145 (53), 131 (23), 119 (28), 91 (23) and 55 (25).

*Diethyl* 1,4-*dimethyl*-2α,3β,5,6,7,8-*hexahydronaphthalene*-2,3-*dicarboxylate* **3n**. Isolated by PLC on silica gel (hexane–acetone 70:30). Oil, b.p. 147 °C (26 Pa) (Found: C, 70.5; H, 8.45. $C_{18}H_{26}O_4$ requires C, 70.59; H, 8.50%); $\nu_{max}$(film)/cm$^{-1}$ 2960, 2860, 1735, 1440, 1270, 1120, 1020 and 800; $\delta_H$(200 MHz; $CDCl_3$) 1.21 (6 H, t, *J* 7.1, 2 × Me), 1.42–1.61 (4 H, m, 2 × $CH_2$), 1.85 (6 H, s, 2 × Me), 1.91–2.18 (2 H, m, allylic CH), 2.27–2.62 (2 H, 2 m, 2 × allylic CH), 3.33 (2 H, s, 2 × CHCO) and 4.09 and 4.10 (4 H, 2 q, *J* 7.1, 2 × $CH_2$); *m/z* 307 ($M^+$ + 1), 306 ($M^+$), 233 (22), 232 (26), 231 (19), 187 (100), 186 (32), 161 (42), 160 (23), 159 (45), 119 (66) and 91 (10).

*Diethyl* 1,1,3,3-*tetramethyl*-2,3,4,5-*tetrahydro*-1H-*isoindole*-5,6-*dicarboxylate* **4**. Isolated by PLC on silica gel (hexane–acetone 70:30). Pale yellow oil, b.p. 129 °C (8 Pa) (Found: C, 67.2; H, 8.4; N, 4.3. $C_{18}H_{27}NO_4$ requires C, 67.29; H, 8.41; N, 4.36%); $\nu_{max}$(film)/cm$^{-1}$ 3340, 2980, 2880, 1735, 1715, 1600, 1470, 1375, 1270, 1105, 1030 and 800; $\delta_H$(200 MHz; $CDCl_3$) 1.07 (3 H, t, *J* 7.1, Me), 1.08, 1.09, 1.13 and 1.14 (12 H, 4 s, 4 × Me), 1.19 (3 H, t, *J* 7.0, Me), 1.77 (1 H, br s, NH), 2.32 (1 H, dd, *J* 17.6, 7.5, C*H*H), 2.70 (1 H, dd, *J* 17.6, 3.5, CH*H*), 3.69 (1 H, dd, *J* 7.5, 3.5, CHCO), 3.99 and 4.14 (4 H, 2 q, *J* 7.0, 7.1, 2 × $CH_2$) and 6.98 (1 H, s, =CH); *m/z* 321 ($M^+$), 306 (100), 232 (73), 188 (20), 144 (21), 86 (20) and 84 (29).

*Ethyl* 1,1,3,3-*tetramethyl*-2,3-*dihydro*-1H-*isoindole*-5-*carboxylate* **5a**. Isolated by PLC on silica gel (hexane–acetone 50:50). Oil, b.p. 148 °C (7 Pa) (Found: C, 72.8; H, 8.5; N, 5.6. $C_{15}H_{21}NO_2$ requires C, 72.87; H, 8.50; N, 5.67%); $\nu_{max}$(film)/cm$^{-1}$ 3340, 2980, 1725, 1610, 1460, 1375, 1270, 1105, 1025 and 790; $\delta_H$(200 MHz; $CDCl_3$) 1.35 (3 H, t, *J* 7.1, Me), 1.42 and 1.43 (12 H, 2 s, 4 × Me), 1.97 (1 H, br s, NH), 4.33 (2 H, q, *J* 7.1, $CH_2$), 7.10 (1 H, dd, *J* 7.9, 0.6, CH), 7.75 (1 H, dd, *J* 1.5, 0.6, CH) and 7.90 (1 H, dd, *J* 7.9, 1.5, CH); *m/z* 247 ($M^+$ absent), 232 (100), 204 (21) and 189 (20).

*Diethyl* 1,1,3,3-*tetramethyl*-2,3-*dihydro*-1H-*isoindole*-5,6-*dicarboxylate* **5b**. Isolated by PLC on silica gel (hexane–acetone 70:30). Crystals, m.p. 69–70 °C (Found: C, 67.7; H, 7.9; N, 4.3. $C_{18}H_{25}NO_4$ requires C, 67.71; H, 7.84; N, 4.39%); $\nu_{max}$(film)/cm$^{-1}$ 3330 (NH), 2980, 1730, 1610, 1460, 1375, 1270, 1100, 1025 and 790; $\delta_H$(200 MHz; $CDCl_3$) 1.25 (6 H, t, *J* 7.1, 2 × Me), 1.51 (12 H, s, 4 × Me), 4.29 (4 H, q, *J* 7.1, 2 × $CH_2$), 4.95 (1 H, br s, NH) and 7.40 (2 H, s, 2 × =CH); *m/z* 319 ($M^+$ absent), 305 (18), 304 (100) and 276 (15).

*Tetramethyl*-5-*phenyl*-2,3-*dihydro*-1,1,3,3-1H-*isoindole* **5c**. Isolated by PLC on silica gel (hexane–acetone 70:30). Crystals, m.p. 53–54 °C (Found: 85.95; H, 8.4; N, 5.5. $C_{18}H_{21}N$ requires C, 86.06; H, 8.37; N, 5.58%); $\nu_{max}$(film)/cm$^{-1}$ 3340, 2980, 2960, 1610, 1580, 1460, 1370, 1290, 1140 and 890; $\delta_H$(200 MHz; $CDCl_3$) 1.51 (12 H, br s, 4 × Me), 2.37 (1 H, br s, NH) and

7.13–7.62 (8 H, m, ArH); *m/z* 251 ($M^+$ absent), 237 (100), 236 (50), 221 (70) and 111 (23).

1,1,3,3-*Tetramethyl*-2,3-*dihydro*-1H-*isoindole*-5-*carbonitrile* **5d**. Isolated by PLC on silica gel (hexane–acetone 80:20). Crystals, m.p. 76–78 °C (Found: C, 77.9; H, 7.9; N, 13.9. $C_{13}H_{16}N_2$ requires C, 78.00; H, 8.00; N, 14.00%); $\nu_{max}$(KBr)/cm$^{-1}$ 3340, 2980, 2220, 1610, 1415, 1380, 1250, 1170, 1130, 1000, 905, 850, 770 and 630; $\delta_H$(200 MHz; $CDCl_3$) 1.46 and 1.50 (12 H, 2 s, 4 × Me), 2.20 (1 H, br s, NH), 7.20 (1 H, dd, *J* 7.8, 0.7, =CH), 7.39 (1 H, dd, *J* 1.4, 0.7, =CH) and 7.54 (1 H, dd, *J* 7.8, 1.4, =CH); *m/z* 200 ($M^+$ absent), 185 (100), 170 (61), 169 (24) and 115 (21).

*Diethyl* 1,1,2,3,3-*pentamethyl*-2,3-*dihydro*-1H-*isoindole*-5,6-*dicarboxylate* **5e**. Isolated by flash chromatography on silica gel (hexane–acetone 70:30). Pale yellow oil, b.p. 157 °C (10 Pa) (Found: C, 68.4; H, 8.0; N, 4.1. $C_{19}H_{27}NO_2$ requires C, 68.47; H, 8.11; N, 4.20%); $\nu_{max}$(film)/cm$^{-1}$ 2980, 1730, 1460, 1370, 1270, 1125, 1100 and 790; $\delta_H$(200 MHz; $C_6D_6$) 0.82 (6 H, t, *J* 7.1, 2 × Me), 0.83 (12 H, s, 4 × Me), 1.85 (3 H, s, NMe), 3.97 (4 H, q, *J* 7.1, 2 × $CH_2$) and 7.73 (2 H, s, 2 × =CH); *m/z* 333 ($M^+$), 319 (50), 318 (100) and 317 (24).

5,5,6,7,7-*Pentamethyl*-2-*phenyl*-6,7-*dihydrobenzo*[1,2-c:4,5-c′]*dipyrrole*-1,3(2H,5H)-*dione* **5f**. Isolated by PLC on silica gel (hexane–acetone 65:35). Yellow crystals, m.p. 204–205 °C (Found: C, 75.4; H, 6.6; N, 8.4. $C_{21}H_{22}N_2O_2$ requires C, 75.45; H, 6.59; N, 8.38%); $\nu_{max}$(film)/cm$^{-1}$ 2980, 2940, 1770, 1720, 1600, 1510, 1250, 1120, 860, 800, 760 and 700; $\delta_H$(200 MHz; $CDCl_3$) 1.38 (12 H, s, 4 × Me), 2.43 (3 H, s, NMe), 7.36–7.52 (5 H, m, Ph) and 7.71 (2 H, s, 2 × =CH); *m/z* 334 ($M^+$), 320 (24), 319 (100), 303 (20) and 156 (20).

4,5,5,6,7,7-*Hexamethyl*-2-*phenyl*-6,7-*dihydrobenzo*[1,2-c:4,5-c′]*dipyrrole*-1,3(2H,5H)-*dione* **5g**. Isolated by PLC on silica gel (hexane–acetone 65:35). Yellow crystals, m.p. 139–140 °C (Found: C, 75.8; H, 6.9; N, 8.0. $C_{22}H_{24}N_2O_2$ requires C, 75.86; H, 6.90; N, 8.05%); $\nu_{max}$(film)/cm$^{-1}$ 2980, 2940, 2800, 1775, 1720, 1600, 1510, 1380, 1255, 1120, 860, 760, 745, 700 and 635; $\delta_H$(200 MHz; $CDCl_3$) 1.37 (6 H, s, 2 × Me), 1.48 (6 H, s, 2 × Me), 2.42 (3 H, s, NMe), 2.82 (3 H, s, Me), 7.31–7.48 (5 H, m, Ph) and 7.58 (1 H, s, =CH); *m/z* 348 ($M^+$), 334 (24), 333 (100), 318 (21) and 317 (23).

4,5,5,6,7,7,8-*Heptamethyl*-2-*phenyl*-6,7-*dihydrobenzo*[1,2-c:4,5-c′]*dipyrrole*-1,3(2H,5H)*dione* **5h**. Isolated by PLC on silica gel (hexane–acetone 45:55). Pale yellow crystals, m.p. 163–164 °C (Found: C, 76.2; H, 7.2; N, 7.7. $C_{23}H_{26}N_2O_2$ requires C, 76.18; H, 7.20; N, 7.74%); $\nu_{max}$(film)/cm$^{-1}$ 2980, 2940, 1770, 1720, 1600, 1380, 1250, 1120 and 800; $\delta_H$(200 MHz; $CDCl_3$) 1.47 (12 H, s, 4 × Me), 2.41 (3 H, s, NMe), 2.82 (6 H, s, 2 × Me) and 7.28–7.52 (5 H, m, Ph); *m/z* 362 ($M^+$), 348 (17), 347 (100) and 332 (17).

2-(*Hex*-4-*ynyl*)-1,3,4-*trimethyl*-5,6,7,8-*tetrahydronaphthalene* **6b**. Isolated by PLC on silica gel (hexane–acetone 90:10). Oil, b.p. 107 °C (10 Pa) (Found: C, 89.5; H, 10.4. $C_{20}H_{28}$ requires C, 89.55; H, 10.45%); $\nu_{max}$(film)/cm$^{-1}$ 2980, 2930, 2860, 2120, 1505, 1440, 830, 810 and 630; $\delta_H$(200 MHz; $CDCl_3$) 1.58–1.81 (8 H, m, 4 × $CH_2$), 1.84 (3 H, t, *J* 2.5, Me), 1.99, 2.04 and 2.10 (9 H, 3 s, 3 × Me), 2.18–2.24 (2 H, m, $CH_2C\equiv$), 2.56 (2 H, t, *J* 7.2, benzylic $CH_2$) and 2.70–2.80 (4 H, m, 2 × endocyclic $CH_2$); *m/z* 268 ($M^+$), 253 (23), 187 (100), 173 (23) and 157 (26).

*Ethyl* 4-[(E)-2-*ethoxycarbonylvinyl*]-2-*methoxycarbonyl*-2,3,4,5,6,7-*hexahydro*-1H-*isoindole*-5-*carboxylate* **7a**. The crude isomer mixture was separated by PLC on silica gel (hexane–acetone 70:30). Only one pure isomer (18% yield based on substrate **1g**) was obtained, as a pale yellow oil, b.p. 128 °C (16 Pa) (Found: C, 65.5; H, 7.1; N, 3.9. $C_{18}H_{25}NO_6$ requires C, 65.44; H, 7.12; N, 3.99%); $\nu_{max}$(film)/cm$^{-1}$ 3000, 2975, 2870, 1735, 1720, 1660, 1460, 1400, 1190, 1120, 1040, 990, 865 and 780; $\delta_H$(200 MHz; $CDCl_3$) 1.22 (3 H, t, *J* 7.1, Me), 1.26 (3 H, t, *J* 7.1, Me), 1.67–2.15 (4 H, m, 2 × $CH_2$), 2.66–2.86 (1 H, m, CHCO), 3.26–3.45 (1 H, m, CHC=), 3.70 (3 H, s, OMe), 3.97–4.28 [8 H, m, 4 × $CH_2$ (2 × $NCH_2$, 2 × $OCH_2$)], 5.76 (1 H, dd, *J* 15.6, 0.8, =CHCO) and 6.73 (1 H, dd, *J* 15.6, 8.6, =CH); *m/z* 351 ($M^+$), 306 (52), 305 (100), 278 (90), 277 (70), 245 (55), 232 (90), 230 (98) and 204 (65).

*Ethyl* 4-[(E)-2-*ethoxycarbonylvinyl*]-1,1,2,3,3-*pentamethyl*-2,3,4α,5α,6,7-*hexahydro*-1H-*isoindole*-5-*carboxylate* **7b**. Only the major isomer was isolated by PLC on neutral $Al_2O_3$ (hexane–ethyl acetate 70:30), in 30% yield based on substrate **1b**. Pale yellow oil, b.p. 157 °C (18 Pa) (Found: C, 69.4; H, 9.1; N, 3.7. $C_{21}H_{33}NO_4$ requires C, 69.42; H, 9.09; N, 3.86%); $\nu_{max}$(film)/cm$^{-1}$ 2980, 2940, 2890, 1740, 1725, 1660, 1475, 1375, 1180, 1040 and 880; $\delta_H$(200 MHz; $CDCl_3$) 1.02, 1.06, 1.08 and 1.10 (12 H, 4 s, 4 × Me), 1.21 and 1.25 (6 H, 2 t, *J* 7.1, 2 × Me), 1.87–2.12 (4 H, m, 2 × $CH_2$), 2.28 (3 H, s, NMe), 2.60 (1 H, dd, *J* 8.7, 4.3, CHCO), 3.49 (1 H, dd, *J* 8.5, 4.3, CHC=), 4.11 and 4.18 (4 H, 2 q, *J* 7.1, 2 × $CH_2$), 5.87 (1 H, dd, *J* 15.5, 0.9, =CHCO) and 6.91 (1 H, dd, *J* 15.5, 8.5, =CH); *m/z* 363 ($M^+$), 350 (25), 349 (100), 348 (58), 136 (20) and 56 (36).

*Ethyl* 4-[(E)-2-*ethoxycarbonylvinyl*]-2,3,4α,5α,6,7-*hexahydroindene*-5-*carboxylate* **7c**. Only the major isomer was isolated by column chromatography on neutral $Al_2O_3$ (hexane–ethyl acetate 70:30), 45% yield based on substrate **1h**. Oil, b.p. 115 °C (12 Pa) (Found: C, 69.8; H, 8.2. $C_{17}H_{24}O_4$ requires C, 69.86; H, 8.22%); $\nu_{max}$(film)/cm$^{-1}$ 2990, 2970, 2920, 2860, 1740, 1725, 1660, 1455, 1375, 1270, 1180, 1040 and 990; $\delta_H$(400 MHz; $CDCl_3$) 1.22 and 1.25 (6 H, t, *J* 7.1, 2 × Me), 1.71–2.25 (10 H, series of m, 5 × $CH_2$), 2.64 (1 H, ddd, *J* 13.1, 5.5, 2.7, CHCO), 3.25 (1 H, dd, *J* 8.8, 5.5, CHC=), 4.11 and 4.15 (4 H, 2 q, *J* 7.1, 2 × $CH_2$), 5.73 (1 H, dd, *J* 15.5, 0.9, =CHCO) and 6.74 (1 H, dd, *J* 15.5, 8.8, =CH); *m/z* 292 ($M^+$), 246 (100), 219 (30), 218 (39), 189 (24), 174 (21), 173 (43), 172 (26), 145 (46), 118 (27) and 91 (37).

*Ethyl* 1,1,2,3,3,4-*hexamethyl*-7-*methylene*-2,3,4α,5α,6,7-*hexahydro*-1H-*isoindole*-5-*carboxylate* **8a**. Two isomers were isolated by PLC on silica gel (chloroform–acetone 72:23). The fastest moving isomer was a pale yellow oil, b.p. 134 °C (12 Pa) (Found: C, 74.2; H, 9.9; N, 4.7. $C_{18}H_{29}NO_2$ requires C, 74.23; H, 9.97; N, 4.81%); $\nu_{max}$(film)/cm$^{-1}$ 2980, 2800, 1735, 1650, 1605, 1470, 1365, 1280, 1170, 1050, 885 and 800; $\delta_H$(400 MHz; $CDCl_3$) 1.01 (3 H, d, *J* 6.8, CH*Me*), 1.14, 1.21, 1.27 and 1.31 (12 H, 4 s, 4 × Me), 1.28 (3 H, t, *J* 7.1, Me), 2.31 (3 H, s, NMe), 2.49 (1 H, dd, *J* 15.1, 2.7, C=CC*H*H), 2.64 (1 H, ddd, *J* 13.4, 4.3, 2.7, CHCO), 2.77 (1 H, dd, *J* 15.1, 13.4, C=CCH*H*), 2.79 (1 H, dq, *J* 4.3, 6.8, C*H*Me), 4.18 (2 H, q, *J* 7.1, $CH_2$) and 4.90 and 5.05 (2 H, 2 br s, $=CH_2$); *m/z* 291 ($M^+$), 290 (13), 277 (30), 276 (100), 262 (46), 188 (34), 172 (26) and 56 (20).

4α,5β-*Isomer* **8a** (second fastest moving band), b.p. 132 °C (12 Pa). (Found: C, 74.15; H, 9.9; N, 4.7. $C_{18}H_{29}NO_2$ requires C, 74.23; H, 9.97; N, 4.81%); $\nu_{max}$(film)/cm$^{-1}$ 2980, 2940, 2800, 1735, 1650, 1605, 1470, 1370, 1285, 1185, 1040, 885 and 800; $\delta_H$(400 MHz; $CDCl_3$) 1.12 (3 H, s, Me), 1.19 (3 H, d, *J* 6.9, CH*Me*), 1.19–1.22 (9 H, m, 3 × Me), 1.31 (3 H, s, Me), 2.29 (3 H, s, NMe), 2.52 (1 H, ddd, *J* 3.4, 4.4, 4.4, CHCO), 2.63–2.74 (2 H, m, $CH_2C$=), 2.89 (1 H, dq, *J* 3.4, 6.9, C*H*Me), 4.04 and 4.09 (2 H, 2 q, *J* 7.1, $CH_2$), 4.89 and 5.04 (2 H, 2 br s, $=CH_2$); *m/z* 291 ($M^+$), 277 (17), 276 (100), 188 (19), 172 (16) and 56 (15).

*Diethyl* 1,1,2,3,3,4-*hexamethyl*-7-*methylene*-2,3,4α,5β,6α,7-*hexahydro*-1H-*isoindole*-5,6-*dicarboxylate* **8b**. Two isomers were isolated by PLC on neutral alumina (hexane–ethyl acetate 80:20). The fastest moving isomer (major) was a pale yellow oil, b.p. 151 °C (12 Pa) (Found: C, 69.35; H, 9.0; N, 3.8. $C_{21}H_{33}NO_4$ requires C, 69.42; H, 9.09; N, 3.86%); $\nu_{max}$(film)/cm$^{-1}$ 2980, 2940, 2800, 1745, 1740, 1650, 1610, 1470, 1380, 1270, 1190, 1040 and 890; $\delta_H$(400 MHz; $CDCl_3$) 1.10, 1.16, 1.20 and 1.30 (12 H, 4 s, 4 × Me), 1.14 (3 H, d, *J* 6.8, CH*Me*), 1.20 and 1.24 (6 H, 2 t, *J* 7.1, 2 × Me), 2.26 (3 H, s, NMe), 2.86 (1 H, dq, *J* 5.4, 6.8,

MeC*H*), 3.03 (1 H, dd, *J* 6.2, 5.4, CHCO), 3.72 (1 H, d pseudo t, *J* 1.2, 6.2, C=CCHCO), 4.11 and 4.16 (4 H, 2 q, *J* 7.1, 2 × $CH_2$), 4.84 (1 H, d, *J* 1.2, =CH) and 5.24 (1 H, 2 br s, =CH); $\delta_C$(25 MHz; $CDCl_3$) 14.07, 14.16, 19.45, 24.47, 24.80, 25.00, 25.12 and 25.73 (8 × Me), 30.90, 49.42 and 50.56 (3 × CH), 60.82 (2 × $CH_2$), 66.12 (2 × qC), 111.68 (=$CH_2$), 134.59, 137.24 and 145.24 (3 × qC) and 173.11 and 173.14 (2 × CO); *m/z* 363 ($M^+$), 349 (15), 348 (100), 318 (15), 274 (18) and 56 (10).

4α,5α,6β-*Isomer* **8b** (second fastest moving band), b.p. 146 °C (12 Pa) (Found: C, 69.4; H, 9.0; N, 3.8. $C_{21}H_{33}NO_4$ requires C, 69.42; H, 9.09; N, 3.86%); $\nu_{max}$(film)/$cm^{-1}$ 2980, 2940, 2800, 1745, 1740, 1650, 1610, 1465, 1380, 1270, 1040 and 885; $\delta_H$(400 MHz; $CDCl_3$) 0.985 (3 H, d, *J* 6.8, CH*Me*), 1.13, 1.17, 1.24 and 1.28 (12 H, 4 s, 4 × Me), 1.25 and 1.29 (6 H, 2 t, *J* 7.1, 2 × Me), 2.28 (3 H, s, NMe), 2.80 (1 H, dq, *J* 5.0, 6.8, MeC*H*), 3.08 (1 H, dd, *J* 12.4, 5.0, CHCO), 3.73 (1 H, ddd, *J* 12.4, 2.6, 2.3, C=CCH), 4.15–4.29 (4 H, q systems, *J* 7.1, 2 × $CH_2$), 4.99 (1 H, d, *J* 2.3, =CH) and 5.20 (1 H, d, *J* 2.6, =CH); *m/z* 363 ($M^+$), 349 (15), 348 (100), 202 (19), 186 (22), 172 (21) and 56 (20).

*Diethyl* 1,1,2,3,3,4-*hexamethyl*-7-*methylene*-2,3,4α,5β,6β,7-*hexahydro*-1H-*isoindole*-5,6-*dicarboxylate* **8c**. Three isomers were separated by PLC on silica gel (hexane–acetone 70:30). Only one pure isomer (40% based on substrate **1c**) was obtained, as a pale yellow oil, b.p. 144 °C (12 Pa) (Found: C, 69.4; H, 9.05; N, 3.8. $C_{21}H_{33}NO_2$ requires C, 69.42; H, 9.09; N, 3.86%); $\nu_{max}$(film)/$cm^{-1}$ 2980, 2940, 2800, 1740, 1735, 1650, 1610, 1468, 1380, 1270, 1040 and 890; $\delta_H$(400 MHz; $CDCl_3$) 1.08–1.29 (21 H, s and m system, 7 × Me), 2.26 (3 H, s, NMe), 2.59 (1 H, dd, *J* 8.5, 4.4, CHCO), 2.95 (1 H, dq, *J* 8.5, 7.1, *CH*Me), 3.64 (1 H, d, *J* 4.4, C=CCHCO), 4.01 and 4.11 (4 H, q system, *J* 7.0, 2 × $CH_2$) and 5.06 and 5.14 (2 H, 2 s, 2 =CH); *m/z* 363 ($M^+$), 349 (18), 348 (100), 290 (41), 274 (22), 172 (16) and 56 (14).

1,1,2,3,3-*Pentamethyl*-4,6-*bis*(*trimethylsilyl*)-2,3-*dihydrocyclopenta*[c]*pyrrol*-5(1H)-*one* **9**. Isolated by crystallization (from hexane–dichloromethane 50:50) as crystals, m.p. 129–130 °C (Found: C, 64.4; H, 9.9; N, 4.1. $C_{18}H_{33}NOSi_2$ requires C, 64.48; H, 9.85; N, 4.18%); $\nu_{max}$(KBr)/$cm^{-1}$ 2990, 2970, 1695, 1600, 1350, 1250, 1225, 880, 850, 790 and 700; $\delta_H$(200 MHz; $CDCl_3$) 0.25 (18 H, s, 6 × Me), 1.32 (12 H, s, 4 × Me) and 2.29 (3 H, s, NMe); *m/z* 335 ($M^+$), 320 (100), 73 (20) and 56 (30).

*Ethyl* 7,10-*dimethylfluoranthene*-8-*carboxylate* **13**. Purified by chromatographic column on silica gel (hexane–acetone 70:30). Pale yellow solid, m.p. 74–75 °C (Found: C, 83.4; H, 5.9. $C_{21}H_{18}O_2$ requires C, 83.44; H, 5.96%); $\nu_{max}$(KBr)/$cm^{-1}$ 2980, 1710, 1600, 1440, 1370, 1280, 1240, 1180, 1055, 825 and 775; $\delta_H$(200 MHz; $CDCl_3$) 1.47 (3 H, t, *J* 7.2, Me), 2.64 (3 H, s, Me), 2.88 (3 H, s, Me), 4.43 (2 H, q, *J* 7.2, $CH_2$), 7.52–7.63 (3 H, m, 2 *meta* CH, =CHCCO), 7.77 and 7.81 (2 H, 2 d, *J* 4.5, 2 *para* CH) and 7.89 and 7.98 (2 H, 2 d, *J* 7.2, 2 *ortho* CH); *m/z* 302 ($M^+$, 100), 273 (26), 257 (23), 256 (67), 229 (32), 228 (88), 226 (62), 201 (26), 113 (23) and 101 (20).

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