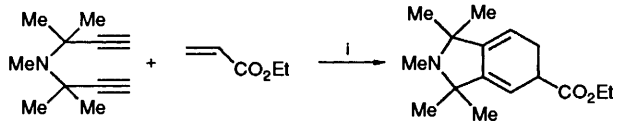
Lewis Acid- or Base-catalysed Double Ring Closure of Diacetylenic Compounds with Activated Olefins†

Zhiming Zhou, Mirco Costa* and Gian Paolo Chiusoli
Istituto di Chimica Organica dell'Università, Viale delle Scienze, I-43100 Parma, Italy

Conformationally rigid 1,6- or 1,7-dialkynes, terminally substituted with one or two alkyl groups, react with activated olefins in the presence of Lewis acids or bases to give a double ring closure to alkylidenecyclohexene compounds. The new reaction involves isomerization of the dialkyne to a cyclic ene-allene, which in its turn reacts with activated olefins regioselectively to give condensed rings.

In the preceding paper[1] we reported the cobalt(0)-catalysed reaction of 1,6- or 1,7-diynes with activated olefins; for example, dialkyne **1b** reacted with ethyl acrylate **2a** under the catalytic action of cobalt(0) complexes to give compound **3g** (Scheme 1).

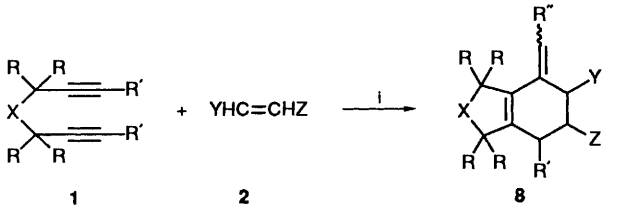


1b **2a** **3g**

Scheme 1 *Reagents and conditions:* i, bis(acetonitrile)bis(diethylfumarate)cobalt (Co^0), 60 °C, toluene

We also reported on several other compounds (**4–13**, see preceding paper) connected with this reaction.

We observed that when compounds **1** contained terminal alkyl substituents, as in the case of diynes **1c**, **1d** and **1f**, new compounds **8** were obtained (Scheme 2) whose formation was



1 **2** **8**

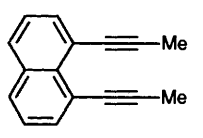
Scheme 2 *Reagents and conditions:* i, Lewis base or acid catalyst, 80 °C, toluene

no longer controlled by cobalt if the latter was used in a less than stoichiometric amount. We therefore undertook a separate study of the reaction in the absence of cobalt (Scheme 2). A brief account appeared recently.[2]

Results

The reaction leading to products **8** (Scheme 2) occurred cleanly at 60–80 °C. Results are reported in Table 1. The same numbers and letters as in the preceding paper are adopted here for those compounds that have been used for the present reaction and new letters are added for new substrates and products.

Other terminally substituted diynes (**1i** and **1j**), not containing geminal methyl groups, were also tested but no reaction ensued even in the presence of bases. We therefore reasoned that



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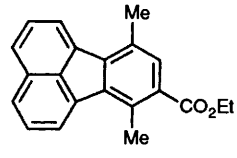

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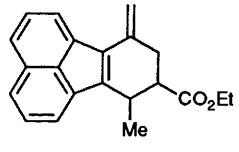

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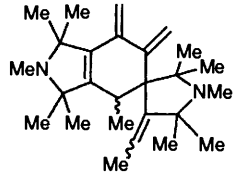

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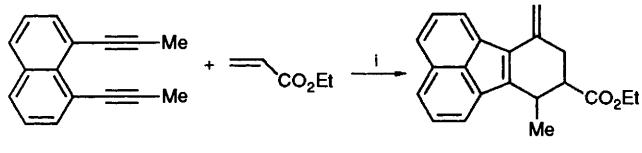
for reactions of the type in Scheme 2 to occur there must be two rigidly held alkyne groups so near to each other that ring closure to a cyclic ene-allene would be preferred to the formation of an open-chained allene (see later). A compound meeting this requirement is **11**. It did not react as such with activated olefins but it did in the presence of a base (2,2,6,6-tetramethylpiperidine, TMP) or an acid (triphenylboron) (Scheme 3).



11 **2a** **14**

Scheme 3 *Reagents and conditions:* i, Lewis base or acid, 80 °C, toluene

The scope of the reaction described here thus includes compounds of both type **1** and type **11**, namely rigidly oriented alkyl-substituted diacetylenic compounds.

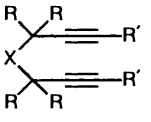
Ethyl acrylate **2a** and diethyl fumarate **2b** reacted with diyne **1c** satisfactorily as well as with the corresponding maleate **2c**, giving two stereoisomers, differing from each other in the relative position of the remaining methyl group and of the adjacent alkoxycarbonyl group (entries 1–3). Assignment of stereochemistry was made on the basis of NMR coupling constants and of stereochemical models. An upfield chemical shift of the *cis* methyl group in respect to the *trans* one in the $MeCHCHCO_2Et$ segment was constantly observed. Literature data,[3,4] referring to non-condensed alkylidenecyclohexenes were also useful. In particular, isomers of compound **8a** were

† Numbering of compounds in this paper corresponds to that in the preceding paper. For example, compounds **6**, **7**, **9**, **10** and **12** are not mentioned in this paper.

Table 1 Reactions of diynes **1** and **11** with olefins **2** (1:2 molar ratio) in toluene (0.4 mol dm^{-3})

Entry	Diyne	Olefin	T/°C	t/h	Conversion (%)[a]	Yield[b]
1	**1c**	**2a**	60	6	92	**8a** 79 (1:1) (35 4α,5β), (34 4α,5α)
2	**1c**	**2b**	60	10	97	**8b** 85 (3:1) (56 4α,5β,6α), (20 4α,5α,6β)
3	**1c**	**2c**	80	24	89	**8c** 73 (4:1.5:1)[c] (40 4α,5β,6β)
4	**1c**	**2f**	80	8	83	**8d** 53 (3:1)[d] (38 4α,5β), (9 4α,5α)
5	**1c**	**2g**	80	6	97	**8e** 87 (1:1) (38 4α,5β), (39 4α,5α)
6	**1c**	**2i**	70	6	95	**8f** 83 (67) (1:1), (34 4α,5α), (33 4α,5β)
7	**1f**	**2a**	80	4	100	**8g** 96 (85)
8	**1f**	**2b**	80	4	96	**8h** 84 (72 5α,6β)
9	**1f**	**2h**	80	8	94	**8i** (13 3aα,4α) + **4a** (63) + **5g** (13)
10	**1c**	**2h**	80	8	86	**8j** (35 3aα,4β,8aα) + **4b** (21 3aα,4α and 13 3aα,4β)
11	**1d**	**2a**	60	8	98	**8k** 95 (1:1) (42 *syn*-4α,5α), (42 *anti*-4α,5α)
12	**1d**	**2b**	60	8	94	**8l** 71 (2:1) (40 *syn*-4α,5α,6β), (20 *anti*-4α,5α,6β)
13	**1d**	**2j**	60	7	79	**8m** 61 (45) (4:1) (33 *syn*-4α,5α,6β), (6 *anti*-4α,5α,6β)
14	**11**	**2a**	120	36	98	**14** 66 (1:1) (7α,8β), (7α,8α)[e]
15	**11**	**2a**	120	36	95	**14** 40 (1:1) (7α,8β), (7α,8α)[f]

[a] Based on substrate **1**, determined by GLC. [b] Based on substrate **1**, determined by GLC; isomer ratios (by GLC) and isolated yields are in parentheses. [c] The third isomer (not isolated) coincides (GLC) with compound **8b** (4α,5β,6α); the second isomer must be **8c** (4α,5α,6α) because of the different retention time from that of compound **8b**. [d] Product **8d** was also transformed and isolated as compound **5i** (40% yield). [e] In the presence of tetramethylpiperidine compound **14** was isolated as the aromatic system **13** (53% yield). [f] In the presence of BPh_3: compound **14** was isolated as the aromatic system **13** (34% yield).



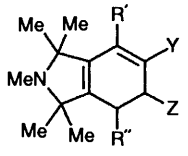
1

1	X	R	R′
b	NMe	Me	H
c	NMe	Me	Me
d	NMe	Me	Et
f	NMe	Me	H, Me
i	CH_2	H	Me
j	CH_2CH_2	H	Me

Y–CH=CH–Z

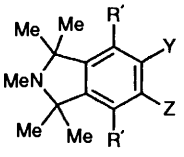
2

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	
i	H	COMe
j	(*E*) Me	CO_2Me



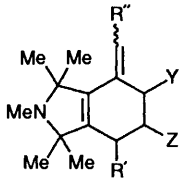
4

4	R′	R″	Y	Z
a	Me	H	OCN(Ph)CO	
b	Me	Me	OCN(Ph)CO	



5

5	R′	Y	Z
g	H, Me	OCN(Ph)CO	
i	Me	H	Ph



8

8	R′	R″	Y	Z
a	Me	H	H	CO_2Et
b	Me	H	CO_2Et	CO_2Et (*trans*)
c	Me	H	CO_2Et	CO_2Et (*cis*)
d	Me	H	H	Ph
e	Me	H	H	CN
f	Me	H	H	COMe
g	H	H	H	CO_2Et
h	H	H	CO_2Et	CO_2Et
i	H	H	OCN(Ph)CO	
j	Me	H	OCN(Ph)CO	
k	Et	Me	H	CO_2Et
l	Et	Me	CO_2Et	CO_2Et
m	Et	Me	Me	CO_2Me

assigned the *trans* and *cis* stereochemistry, respectively, because only those assignments were compatible with the *J*-values observed. In both isomers the protons of the Me*CHCH*CO_2Et groups exhibit small *J*-values (3.4 and 4.3 Hz, respectively) but only in the *cis* one were two protons of the group $EtO_2CCHCHH$ coupled with a large *J*-value (13.4 Hz), corresponding to an axial arrangement. This isomer must therefore be assigned the *cis* structure and consequently the

other isomer is the *trans* one. Analogous reasoning leads to the assignment of the *trans*:*trans* (4α,5β,6α) configuration to the major isomer (3:1 ratio) of product **8b** (resulting from the reaction of diyne **1c** with diethyl fumarate **2b**) whose MeC*H*C*H*CO_2Et and EtO_2CC*H*C*H*CO_2Et protons have small *J*-values (5.4 and 6.2 Hz, respectively), corresponding to equatorial protons. On the other hand, compound **8b** [*cis*,*trans*-isomer (4α,5α,6β)] has equatorial (*J* 5.0 Hz) and axial (*J* 12.4 Hz) protons. The stereochemistry of the starting olefin is retained, so compound **8c** (from the reaction of diyne **1a** with diethyl maleate **2c**) is mainly *trans*,*cis* (4α,5β,6β), the above protons being axial (*J* 8.5 Hz) and equatorial (*J* 4.4 Hz), respectively. The minor isomer (4α,5β,6α, 1.5:4 ratio to the former) could not be isolated. A third isomer has the same GLC retention time as one of the isomers of compound **8b** and is likely to result from previous maleate-to-fumarate isomerization.

The dipropargylamine **1c** also reacts with styrene **2f**, acrylonitrile **2g** and methyl vinyl ketone **2i**, to give two isomers in each case, respectively (**8d** 3:1, **8e** 1:1 and **8f** 1:1, entries 4–6).

The major isomer of product **8d** (entry 4) is the *trans* one (3:1 to the *cis*). Coupling constants could not be read but they were clear for the *cis* isomer (*J* 2.9 and 13.6 Hz, respectively, for the 3α,4β and 4β,5α protons).

The two isomers of compound **8e** (1:1, entry 5) were assigned *trans* and *cis* configurations, according to the same criteria as for the aforementioned products.

Isomers of compound **8f** (1:1, entry 6) were assigned the *trans* and *cis* structure on the basis of the smaller *J*-values of the former (3.2 and 2.3 Hz) compared with those of the latter (3.8, 12.2 Hz).

The formation of compounds **8g–i** (from the reaction of terminally monomethyl-substituted dialkyne **1f** with ethyl acrylate **2a**, diethyl fumarate **2b** and *N*-phenylmaleimide **2h**, respectively, entries 7–9) confirms the regioselectivity and stereospecificity of the reaction. In the last case, however, isomerization to compound **4a** by exocyclic double-bond shift to the internal position and aromatization to compound **5g** took place to a large extent.

Compound **8j** (from the reaction of diyne **1c** with *N*-phenylmaleimide **2h**, entry 10) has the 3aα,4β,8aβ structure, analogous to the major isomer of compound **8c**. In this case, however, the exocyclic double-bond shift to the internal position, leading to compound **4b**, was particularly favoured. Two isomers of compound **4b** were isolated in ~2:1 ratio. The *J*-values of the former were read without difficulty so that the *trans* structure could be assigned to it.

Passing now to compounds **8k–m** (from the reaction of diyne **1d** with ethyl acrylate **2a**, diethyl fumarate **2b** and methyl crotonate **2e**, respectively, entries 11–13) one has to take into account the fact that an additional stereochemical arrangement arises from the *syn* or *anti* position (in respect to the vinyl substituent of the exocyclic double bond; *E*,*Z* symbols are not used here for the sake of clarity) of the ethylidene methyl group, so four isomers can be expected. Essentially two isomers were isolated in all cases, however, showing similar *J*-values and differing in the δ-values of the ethylidene protons. The *J*-values were consistent with the *cis* (4α,5α) structure of both isomers, so the latter have *syn* or *anti* configurations. The problem of which is which could be solved for compound **8k** on the basis of ^{1}H and ^{13}C NMR spectroscopy: an upfield shift of the ^{13}C CH_2 absorption characterizes the minor isomer, containing the methyl group on the same side as the CH_2 (*anti* to the vinyl substituent of the exocyclic double bond). It is also noteworthy that the ^{1}H NMR spectrum shows the opposite trend (downfield shift) for the axial CH_2 proton. Analogous trends are observed for compounds **8l** and **8m**. Other useful information comes from literature data.[3,4] The δ-value for the *syn* isomer of compound **8l** (5.18, H *anti*) is consistent with that of the unsubstituted methylene of compound **8a** (5.04) and with the literature[3] values for *anti* 3 H protons in methylenecyclohexene compounds such as the dimethyl esters of 1α,2β,6α- and 1β,2α,6α-3-methylene-6-propylcyclohex-4-ene-1,2-dicarboxylic acid (δ 4.89 and 4.80, respectively) and for their ethylidene *E* (our *syn*) homologues (at δ 5.28, 5.12). The marked change in δ on passing to the *anti* isomer of compound **8l** (5.80, H *syn*) is to be compared with the downfield shift reported in the literature[3] for the above mentioned ethylidene compounds (*e.g.*, from δ 5.12 to δ 5.65, H *syn*). Since the most abundant isomer of compound **8b** corresponds to the *syn* one (also in agreement with literature data[3]) the *syn* structure can be reasonably assigned not only to the most abundant isomer of compound **8k** (already identified as mentioned above) but reasonably also to that of compound **8m**, for which the δ-values of the *syn* and *anti* isomers of (5.37, 5.48 for H *anti* and *syn*, respectively) follow the same trend but are not so different.

Interestingly, in the absence of added olefin, dimers of diynes **1** are slowly formed. On heating, compound **15** was isolated from the dimerization of diyne **1c**. Its structure is in agreement with NMR data (see Experimental section). The stereochemistry could not be assigned. Three other isomers were present, however, in the GLC peak areas proportions of 0.25:0.10:0.25, relative to **15** as 1.0.

The use of substrate **11** (entries 14 and 15) led us to establish that the reaction occurs in the presence of either an amine (2,2,6,6-tetramethylpiperidine, TMP) or a Lewis acid (triphenylboron). The same two isomers of compound **14**, in 1:1 ratio, were obtained in both cases with the same regioselectivity observed for the analogous compounds **8**. ^{1}H NMR absorptions of the exocyclic methylene protons in the reaction product were observed at δ 5.12, 5.19, 5.57 and 5.76. The isomers were transformed into the aromatic compound **13** by dehydrogenation on Pd/C at 140 °C.

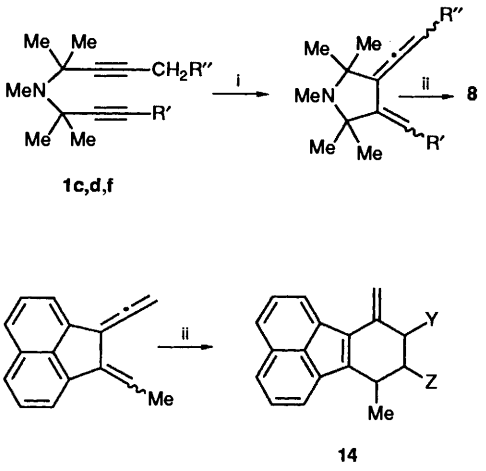
The following general observations can be drawn from these results: (a) terminal olefins CH_2=CHZ react regioselectively with diynes **1** or **11** to give compounds **8** or **14**, containing the Z substituent in the position farthest from the alkylidene group (entries 1, 4–7, 11, 13–15); (b) from the stereochemical point of view the reaction gives mixtures of stereoisomers, corresponding to *trans* to *cis* ratio of ~1:1 (entries 1, 5, 6, 11, 13, 15), with the exception of the product from styrene **2f** for which the ratio is 3:1. A more complex situation arises when olefins with two electron-withdrawing substituents are used. While their stereochemistry is preserved, the terminal methyl group of the starting dialkyne (not transformed into an alkylidene group) becomes, to a large extent, *trans* to the substituent on the adjacent carbon atom of the product. When, however, an ethyl group is present on both the terminal carbons of the triple bonds (compound **1d**) the reaction with acrylic, fumaric or crotonic esters **2a**, **2b** or **2j** causes the group to become *cis* stereoselectively. Two isomers are generated, depending on the *syn* or *anti* position of the substituent on the exocyclic methylene.

The reaction products can be isomerized to equilibrium mixtures by treatment with 25% NaOEt in ethanol. Thus both isomers of compound **8a** gave a 5:3 *trans*:*cis* ratio after isomerization. With diethyl fumarate **2b** and disubstituted olefins, however, alkaline isomerization first leads to mobilization of the C–H near to the C=CH_2 group, with formation of compounds of type **4**.

Discussion

The reaction can be interpreted as the result of a base- or acid-catalysed isomerization,[5] followed by a Diels–Alder-type reaction (Scheme 4).

An intermediate forms slowly from substrates **1c**, **1d** and **1f** on



Scheme 4 *Reagents:* i, TMP or BPh_3 (TMP = 2,2,6,6-tetramethylpiperidine); ii, **2**

storage and, in the absence of other olefins, dimerizes to compounds of type **15**. It appears on GLC as a transient peak which is too close to that of substrate **1** to allow it to be separated from it. It is to be noted that isomerization to a cyclic ene-allene and not isomerization to a simple allene group must occur in this situation, because in the latter case the reaction leading to product **8** does not take place. Thus the use of isomerizing agents (Bu^{t}OK) causes acetylene–allene isomerization of one or both the alkynyl groups and does not lead to product **8**. In order for the desired reaction to occur it is necessary that cyclization takes place before the proton recombines with the unsaturated carbon. This condition seems to be met when nitrogen bases are used and geminal alkyl groups are present *alpha* to the triple bonds. These groups orient the triple bonds in the correct way to induce ring formation.[1]

Another favourable condition for cyclization is offered by substrates in which two acetylenic groups are rigidly held parallel as in the case of 1,8-dipropynylnaphthalene **11**.

A variety of olefins, conjugated to electron-withdrawing groups, can react with the cyclic ene-allene system. If, for steric or electronic reasons, they react too slowly, dimerization (*e.g.*, to **15** from **1c**) is preferred.

The cycloaddition step of monosubstituted olefins turns out to be highly regioselective, the olefin substituent invariably being found nearest to the alkyl group R′ that has not been transformed into a vinylidene group. This is in agreement with a Diels–Alder-type reaction.[6] The use of an unsymmetrically disubstituted olefin such as methyl crotonate **2e** also leads to a regioselective reaction, the methoxycarbonyl group being near to the alkyl group and far from the alkylidene group. From the stereochemical point of view the reaction is stereospecific insofar as the relative position of substituents in disubstituted olefins is retained. If a methyl group R′ is present, its position in respect to adjacent groups deriving from mono- or di-substituted olefins gives rise to two stereoisomers. This behaviour is reminiscent of the cyclization of open-chained ene-allene systems, which has been shown to mimic a Diels–Alder-type reaction.[3,4] For the sake of comparison we investigated the reaction of methyl vinyl ketone **2i**, which is the same dienophile as that used for the reaction with ene-allene CH_2=C=CHC(Me)=CHMe.[4] The *trans*-to-*cis* ratio found by those authors was 1:4 while in our case it turns out to be near to 1:1. Assuming that our reaction is of the same type, one can argue that the presence of the condensed ring influences, in approximately the same way, both the *endo* and the *exo* approach of the dienophile to the diene systems. This behaviour was observed by us also with other monosubstituted dienophiles (entries 1, 5, 13, 14) except styrene **2f**, which gave a *trans*-to-*cis* ratio of 3:1 (entry 4). The tendency towards *trans* arrangement is further enhanced by a second substituent such as in fumarate or maleate (entries 2, 3). As expected, these olefins preserve their stereochemistry. Terminally ethyl-substituted dialkynes display very different behaviour, wherein the methyl substituent not converted into the exocyclic ethylidene is preferentially *cis*. A terminal propyl substituent in acyclic ene-allenes was recently shown[3] to assume a *trans* configuration in the reaction product with a fumaric diester as dienophile. The ethyl substituent of the exocyclic double bond was mainly *syn* with respect to the cyclohexylidene double bond. These results are quite different from ours (*cis,syn*:*cis,anti* 2:1). probably because in our case it is the combined action of the allene substituent and of the adjacent ring that determines the stereochemistry of the transition state by allowing only one way of approach of the dienophile to the diene. A detailed mechanistic study, which is outside the scope of the present work, would be required to clarify this point.

The considerations reported above apply to kinetic control of the reaction. This was shown to be the case for the products obtained from open-chained ene-allene systems[4] since the reaction products were found to isomerize in the thermodynamically controlled mixture. In our case too the system is under kinetic control. As an example, with substrates **1** and ethyl acrylate **2a** no significant variation of the isomer ratio was observed with time, while isomerization of either isomer with sodium ethoxide in ethanol gave a 5:3 *trans*-to-*cis* mixture. With disubstituted olefins (fumarate) the most mobile hydrogen is the one on the ethoxycarbonyl-substituted carbon adjacent to the CH_2=C function. As a result the double bond shifted inside the ring with formation of compounds of type **4**.

In conclusion the reaction we have described derives from a combination of cycloisomerization and a Diels–Alder reaction, and exhibits a high regioselectivity, while its stereoselectivity can be controlled by suitable substituents.

Experimental

Equipment and starting materials as well as identification and separation procedures were the same as in the preceding paper.[1]

Reaction of Diynes **1c**, **1d** *and* **1f**, *with Olefins* **2**.—In a typical experiment compound **1c** (306 mg, 1.6 mmol), diethyl fumarate **2b** (550 mg, 3.2 mmol), and some toluene (to adjust the diyne concentration to 4 mol dm^{-3}), were placed under N_2 in a flask equipped with a side-arm and a magnetic bar. The reaction mixture was kept at 60 °C and stirred for 10 h. At 97% conversion of substrate **1c** an 85% yield of two isomers (3:1 ratio) of product **8b** (494 mg, 1.36 mmol) was determined by GLC. After distillation of residual diethyl fumarate **2b** at reduced pressure the two isomers were separated by PLC on alumina (hexane–ethyl acetate 80:20).

Dimerization of Substrate **1c**.—Substrate **1c** (288 mg, 1.5 mmol) was caused to react in toluene (4 cm^3) in a flask under nitrogen. The stirred reaction mixture was kept at 100 °C for 12 h. Substrate **1c** gave a conversion of 68% and four isomers of product **15** were determined by GLC in yields of 21, 5, 2 and 5%. Most of the substrate **1c** was found to have isomerized (isomers not isolated). After distillation of toluene at reduced pressure, the mixture was separated by PLC on silica gel (hexane–acetone 80:20). The major isomer was isolated (41 mg, 14% yield based on substrate **1c**).

Reaction of Diyne **11** *with Olefin* **2a** *in the Presence of a Lewis Acid or Base as Catalyst*.—In a typical experiment diyne **11** (163

mg, 0.8 mmol), TMP (113 mg, 0.8 mmol), ethyl acrylate **2a** (160 mg, 1.6 mmol), and some toluene (to adjust the diyne concentration to 4 mol dm^{-3}), were placed under N_2 in a flask equipped with a side-arm and a magnetic bar. The reaction mixture was stirred at 120 °C for 36 h. At 98% conversion of substrate **11** a 66% yield of two isomers (1:1) of product **14** (161 mg, 1.53 mmol) was determined by GLC. After distillation of residual ethyl acrylate at low pressure, the residue was dissolved in PhCl (5 cm^3), 10% Pd on C was added, and the mixture was stirred at 140 °C for 24 h. The aromatic derivative **12** was separated by column chromatography on silica gel (hexane–acetone 70:30). The same procedure was followed with similar results (Table 1) using BPh_3 as catalyst in a 1:1 ratio to the substrate.

Isomerization Reactions.—Products **8** were caused to isomerize under the action of 10% NaOEt in ethanol. The reaction was continued until the change in product composition was substantially complete. The solution was then neutralized with an excess of saturated aqueous NH_4Cl and the products were extracted with diethyl ether and analysed by GLC.

Properties of Products.—5,5,6,6,7,7,8-*Hexamethyl*-2-*phenyl*-4,5,6,7-*tetrahydrobenzo*-[1,2-c:4,5-c′]*dipyrrole*-1,3-(2H,3aH)-*dione* **4a**. Isolated by PLC on silica gel (hexane–acetone 65:35) as crystals, m.p. 132–133 °C (Found: C, 75.4; H, 7.4; N, 7.9. $C_{22}H_{26}N_2O_2$ requires C, 75.43; H, 7.43; N, 8.00%); ν_{max}(film)/cm^{-1} 2980, 1765, 1705, 1590, 1375, 1285, 1145 and 1115; δ_H(200 MHz; $CDCl_3$) 1.21, 1.24, 1.26 and 1.32 (12 H, 4 s, 4 × Me), 2.30 (3 H, s, NMe), 2.50 (3 H, d, *J* 1.4, Me), 2.62 (1 H, dd, *J* 17.5, 13.8, C*H*H), 2.70 (1 H, dd, *J* 17.5, 8.3, CH*H*), 3.68 (1 H, ddd, *J* 13.8, 8.3 and 1.4, CHCO) and 7.25–7.49 (5 H, m, Ph); *m*/*z* 349 (M^+ − 1), 336 (21), 335 (100), 334 (80), 332 (20), 172 (21), 101 (26) and 56 (20).

4,5,5,6,7,7,8-*Heptamethyl*-2-*phenyl*-4α,5,6,7-*tetrahydrobenzo*-[1,2-c:4,5-c′]*dipyrrole*-1,3(2H,3aαH)-*dione* **4b**. Isolated by PLC on silica gel with hexane–acetone (45:55) as developer. *Fastest moving isomer*, pale yellow crystals, m.p. 134–135 °C (Found: C, 75.8; H, 7.6; N, 7.6. $C_{23}H_{28}N_2O_2$ requires C, 75.82; H, 7.69; N, 7.69%); ν_{max}(film)/cm^{-1} 2980, 2940, 2800, 1770, 1705 (CO), 1590, 1500, 1460, 1375, 1115, 865, 750, 700 and 620; δ_H(200 MHz; $CDCl_3$) 0.97 (3 H, d, *J* 6.8, Me), 1.19, 1.22, 1.25 and 1.35 (12 H, 4 s, 4 × Me), 2.30 (3 H, s, NMe), 2.52 (3 H, d, *J* 2.2, Me), 2.89 (1 H, dq, *J* 6.8, 6.8, C*H*Me), 3.72 (1 H, dq, *J* 6.8, 2.2, CHCO) and 7.28–7.49 (5 H, m, Ph); *m*/*z* 364 (M^+), 351 (18), 350 (82), 349 (100), 200 (21), 186 (18) and 108 (23).

3aα,4β-*Isomer of* **4b**. Isolated by PLC on silica gel with hexane–acetone (45:55). Second fastest moving band, pale yellow crystals, m.p. 129–130 °C (Found: C, 75.8; H, 7.7; N, 7.6%); ν_{max}(film)/cm^{-1} 2980, 2940, 2800, 1770, 1705, 1590, 1500, 1460, 1375, 950, 870, 750 and 700; δ_H(200 MHz; $CDCl_3$) 1.09 (3 H, d, *J* 6.8, Me), 1.23, 1.27 and 1.37 (12 H, 3 s, 4 × Me), 2.29 (3 H, s, NMe), 2.58 (3 H, s, Me), 2.91 (1 H, dq, *J* 6.2, 6.8, C*H*Me), 3.45 (1 H, d, *J* 6.2, CHCO) and 7.05–7.42 (5 H, m, Ph); *m*/*z* 364 (M^+), 350 (75), 349 (100), 200 (24), 108 (18) and 56 (18).

Compound **5g** was reported in the preceding paper.[1]

1,1,2,3,3,4,7-*Heptamethyl*-5-*phenyl*-2,3-*dihydro*-1H-*isoindole* **5i**. Isolated by PLC on silica gel with hexane–acetone (75:25) as developer. Crystals, m.p. 69–70 °C (Found: C, 85.9; H, 9.2; N, 4.7. $C_{21}H_{27}N$ requires C, 86.01; H, 9.22; N, 4.78%); ν_{max}(KBr)/cm^{-1} 2980, 2960, 1600, 1575, 1485, 1360, 1290, 1220, 1120, 970, 830, 770 and 710; δ_H(200 MHz; C_6D_6) 1.13 and 1.15 (12 H, s, 4 × Me), 2.02 (6 H, s, 2 × Me), 2.04 (3 H, s, NMe), 6.72 (1 H, s, =CH) and 6.92–7.02 (5 H, m, Ph); *m*/*z* 293 (M^+), 278 (100), 263 (51), 262 (25), 248 (21), 232 (20), 131 (27) and 56 (24).

Compounds **8a–c** and **13** were reported in the preceding paper.[1]

1,1,2,3,3,4-*Hexamethyl*-7-*methylene*-5-*phenyl*-2,3,4α,5β,6,7-*hexahydro*-1H-*isoindole* **8d**. Two isomers were isolated by PLC on silica gel with hexane–acetone (3:1) as developer. The major isomer (fastest moving) was an oil, b.p. 142 °C (8 Pa) (Found: C, 85.3; H, 9.8; N, 4.6. $C_{21}H_{29}N$ requires C, 85.42; H, 9.83; N, 4.75%); ν_{max}(film)/cm^{-1} 2970, 2940, 2890, 1650, 1605, 1460, 1365, 1280, 1135, 975, 890, 760 and 700; δ_H(400 MHz; C_6D_6) 0.91, 1.16, 1.36 and 1.41 (12 H, 4 s, 4 × Me), 1.06 (3 H, d, *J* 6.9, Me), 2.21 (3 H, s, NMe), 2.51–2.58 (2 H, group of signals, C*H*Ph, C*H*Me), 2.62–2.72 (2 H, m, CH_2), 4.87 (1 H, d, *J* 1.3, =CH), 5.12 (1 H, d, *J* 1.2, =CH) and 7.06–7.22 (5 H, m, Ph); *m*/*z* 296 (M^+ + 1), 281 (13), 280 (100), 278 (15), 148 (27), 91 (16) and 56 (22).

4α,5α-*Isomer of* **8d**. The second fastest moving isomer was an oil, b.p. 136 °C (8 Pa) (Found: C, 85.3; H, 9.8; N, 4.6%); ν_{max}(film)/cm^{-1} 2980, 2940, 2890, 1650, 1600, 1460, 1365, 1280, 1135, 975, 890, 760 and 700; δ_H(400 MHz; C_6D_6) 0.78 (3 H, d, *J* 6.9, Me), 1.12, 1.15, 1.40 and 1.46 (12 H, 4 s, 4 × Me), 2.27 (3 H, s, NMe), 2.35 (1 H, dd, *J* 14.4, 2.4, =CC*H*H), 2.42–2.50 (1 H, m, C*H*Me; after decoupling from Me, d, *J* 2.9, 2.94 (1 H, ddt, *J* 13.6, 14.4 and 1.2, C=CCH), 3.05 (1 H, ddd, *J* 13.6, 2.4 and 2.9, C*H*Ph), 4.90 (1 H, br s, =CH), 5.16 (1 H, br s, =CH) and 7.05–7.25 (5 H, m, Ph); *m*/*z* 296 (M^+ + 1), 291 (M^+), 281 (13), 280 (100), 278 (20), 148 (32), 91 (15) and 56 (24).

1,1,2,3,3,4-*Hexamethyl*-7-*methylene*-2,3,4α,5α,6,7-*hexahydro*-1H-*isoindole*-5-*carbonitrile* **8e**. Two isomers were isolated by PLC on silica gel with hexane–acetone (7:3) as developer. The fastest moving isomer was a solid, m.p. 87–88 °C (Found: C, 78.6; H, 9.7; N, 11.4. $C_{16}H_{24}N_2$ requires C, 78.69; H, 9.84; N, 11.48%); ν_{max}(KBr)/cm^{-1} 2980, 2940, 2245, 1650, 1600, 1445, 1365, 1280, 1135, 890 and 740; δ_H(400 MHz; $CDCl_3$) 1.09, 1.19, 1.24 and 1.28 (12 H, 4 s, 4 × Me), 1.32 (3 H, d, *J* 6.9, Me), 2.28 (3 H, s, NMe), 2.58 (1 H, br d, *J* 14.8, C=CC*H*H), 2.66 (1 H, dq, *J* 4.0, 6.9, C*H*Me), 2.81 (1 H, dddd, *J* 14.8, 13.0, 2.1 and 1.2, H_2C=CCH*H*), 2.85 (1 H, dd, *J* 4.0, 13.0, CHCN), 4.93 (1 H, br s, HC=) and 5.13 (1 H, br s, HC=); δ_H(400 MHz; C_6D_6) 0.83, 0.97, 1.17 and 1.24 (12 H, 4 s, 4 × Me), 1.03 (3 H, d, *J* 6.9, Me), 2.12 (3 H, s, NMe), 2.04–2.16 (3 H, group of signals, H_2C=CC*H*H, CHCN, C*H*Me), 2.21 (1 H, dddd, *J* 14.8, 13.4, 2.1 and 1.2, H_2C=CCH*H*), 4.60 (1 H, dd, *J* 2.1, 1.2, =CH) and 4.94 (1 H, d, *J* 2.1, =CH); *m*/*z* 245 (M^+ + 1), 229 (82), 228 (100), 213 (13), 149 (15), 56 (46) and 49 (22).

4α,5β-*Isomer of* **8e**. The second fastest moving isomer was a solid, m.p. 63–64 °C (Found: C, 78.6; H, 9.7; N, 11.4%); ν_{max}(KBr)/cm^{-1} 2980, 2940, 2800, 2245, 1650, 1605, 1465, 1365, 1285, 1135 and 890; δ_H(400 MHz; $CDCl_3$) 1.15, 1.19, 1.29 and 1.32 (12 H, 4 s, 4 × Me), 1.24 (3 H, d, *J* 7.0, Me), 2.30 (3 H, s, NMe), 2.51 (1 H, ddd, *J* 15.0, 3.8 and 1.0, H_2C=CC*H*H), 2.70 (1 H, dq, *J* 3.0, 7.0, C*H*Me), 2.76 (1 H, ddd, *J* 4.0, 3.8 and 3.0, CHCN), 2.81 (1 H, ddd, *J* 15.0, 4.0 and 2.0, H_2C=CCH*H*), 4.99 (1 H, d, *J* 1.0, HC=) and 5.21 (1 H, d, *J* 2.0, HC=); δ_H(400 MHz; C_6D_6) 0.68 (3 H, d, *J* 7.0, Me), 1.04, 1.07, 1.30 and 1.33 (12 H, 4 s, 4 × Me), 1.93 (1 H, ddd, *J* 4.0, 3.8 and 3.0, CHCN), 2.02 (1 H, ddd, *J* 15.0, 3.8 and 1.0, H_2C=CC*H*H), 2.16 (3 H, s, NMe), 2.17 (1 H, dq, *J* 3.0, 7.0, C*H*Me), 2.27 (1 H, dddd, *J* 15.0, 4.0, 2.0 and 2.0, H_2C=CCH*H*), 4.77 (1 H, dd, *J* 1.0, 2.0, =CH) and 5.12 (1 H, d, *J* 2.0, =CH); *m*/*z* 245 (M^+ + 1), 244 (M^+), 229 (48), 228 (100) and 56 (47).

5-*Acetyl*-1,1,2,3,3,4-*hexamethyl*-7-*methylene*-2,3,4α,5α,6,7-*hexahydro*-1H-*isoindole* **8f**. Isolated by PLC on alumina with hexane–acetone (70:30) as developer. Fastest moving isomer was an oil, b.p. 106 °C (8 Pa) (Found: C, 78.1; H, 10.3; N, 5.3. $C_{17}H_{27}NO$ requires C, 78.16; H, 10.34; N, 5.36%); ν_{max}(film)/cm^{-1} 3120, 2980, 2940, 1720, 1650, 1610, 1480, 1370, 1290, 1170, 1035, 980, 920, 885 and 750; δ_H(400 MHz; $CDCl_3$) 0.93 (3 H, d, *J* 6.8, Me), 1.14, 1.17, 1.18 and 1.28 (12 H, 4 s, 4 × Me), 2.17 (3 H, s, COMe), 2.28 (3 H, s, NMe), 2.36 (1 H, br d, *J* 12.2, H_2C=CC*H*H), 2.67 (1 H, dq, *J* 3.8, 6.8, C*H*Me), 2.75–2.81 (2 H, m, CHCO, H_2C=CCH*H*), 4.87 (1 H, s, =CH) and 5.04

(1 H, d, *J* 1.0, =CH); *m/z* 261 (M^+), 247 (39), 246 (100), 202 (18), 188 (21) and 56 (26).

4α,5β-*Isomer of* **8f** (*Second fastest moving band*). B.p. 109 °C (8 Pa) (Found C, 78.1; H, 10.3; N, 5.25%); ν_{max}(film)/cm^{-1} 2980, 2940, 1720, 1650, 1610, 1480, 1370, 1295, 1175, 1035, 980, 915, 885 and 750; δ_H(400 MHz; $CDCl_3$) 1.13, 1.19, 1.24 and 1.27 (12 H, 4 s, 4 × Me), 1.16 (3 H, d, *J* 6.9, Me), 2.11 (3 H, s, COMe), 2.26 (3 H, s, NMe), 2.46 (1 H, ddd, *J* 4.7, 3.2 and 2.3, CHCO), 2.57 (1 H, dd, *J* 15.1, 4.7, H_2C=CC*H*H), 2.62–2.70 (1 H, m, H_2C=CCH*H*), 2.86 (1 H, dq, *J* 3.2, 6.9, C*H*Me) and 4.87 and 5.02 (2 H, 2 br s, =CH_2); *m/z* 261 (M^+), 247 (30), 246 (100), 188 (33), 172 (22), 163 (17), 148 (20) and 56 (28).

Ethyl 1,1,2,3,3-*pentamethyl*-7-*methylene*-2,3,4,5,6,7-*hexahydro*-1H-*isoindole*-5-*carboxylate* **8g**. Isolated by PLC on silica gel with chloroform–acetone (77:23) as developer. Oil, b.p. 127 °C (10 Pa) (Found: C, 73.6; H, 9.7; N, 5.0. $C_{17}H_{27}NO_2$ requires C, 73.65; H, 9.75; N, 5.05%); ν_{max}(film)/cm^{-1} 2980, 2940, 2800, 1740, 1655, 1615, 1470, 1370, 1280, 1170, 1040, 950 and 890; δ_H(200 MHz; $CDCl_3$) 1.10 (6 H, s, 2 × Me), 1.24 and 1.27 (6 H, 2 s, 2 × Me), 1.25 (3 H, t, *J* 7.1, Me), 2.30 (3 H, s, NMe), 2.26–2.37 (2 H, m, CH_2), 2.49–2.65 (3 H, group of m, CH_2, CH), 4.13 (2 H, q, *J* 7.1, CH_2) and 4.85 and 5.00 (2 H, 2 br s, =CH_2); *m/z* 277 (M^+), 262 (100), 248 (46), 201 (18), 174 (35) and 56 (16).

Diethyl 1,1,2,3,3-*pentamethyl*-7-*methylene*-2,3,4,5α,6β,7-*hexahydro*-1H-*isoindole*-5,6-*dicarboxylate* **8h**. Isolated by PLC on silica gel (hexane–acetone 60:40). Pale yellow oil. B.p. 144 °C (10 Pa) (Found: C, 68.7; H, 8.8; N, 4.0. $C_{20}H_{31}NO_4$ requires C, 68.77; H, 8.88; N, 4.01%); ν_{max}(film)/cm^{-1} 2980, 2940, 1745, 1740, 1650, 1610, 1470, 1380, 1270, 1190, 1040 and 890; δ_H(200 MHz; $CDCl_3$) 1.06 and 1.08 (6 H, 2 s, 2 × Me), 1.20 and 1.23 (6 H, 2 t, *J* 7.1, 2 × Me), 1.23 and 1.25 (6 H, 2 s, 2 × Me), 2.28 (3 H, s, NMe), 2.33 and 2.45 (2 H, m, CH_2), 3.16 (1 H, ddd, *J* 7.5, 6.4 and 4.8, C*H*CH_2), 3.62 (1 H, ddd, *J* 7.5, 1.2 and 1.3, CHC=), 4.00 and 4.27 (4 H, 2 q, *J* 7.1, 2 × CH_2), 4.89 (1 H, d, *J* 1.3, =CH) and 5.16 (1 H, br s, =CH); *m/z* 349 (M^+), 335 (100), 334 (79), 260 (26), 188 (23), 172 (24) and 56 (16).

5,5,6,7,7-*Pentamethyl*-8-*methylene*-2-*phenyl*-4,5,6,7,8,8a-*hexahydrobenzo*[1,2-c:4,5-c′]*dipyrrole*-1,3(2H,3aαH)-*dione* **8i**. Isolated by PLC on silica gel (hexane–acetone 65:35). Pale yellow solid, m.p. 106–107 °C (Found: C, 75.4; H, 7.4; N, 7.9. $C_{22}H_{26}N_2O_2$ requires C, 75.43; H, 7.43; N, 8.00%); ν_{max}/(KBr)cm^{-1} 2980, 2940, 2800, 1785, 1720, 1600, 1500, 1460, 1385, 1300, 1185, 900, 750 and 700; δ_H(200 MHz; $CDCl_3$) 1.05, 1.10, 1.20 and 1.32 (12 H, 4 s, 4 × Me), 2.28 (3 H, s, NMe), 3.05–3.17 (2 H, m system, CH_2), 3.19 (1 H, dd, *J* 8.4, 1.2, C*H*CH_2), 3.83 (1 H, d, *J* 8.4, H_2C=CC*H*), 5.40 and 5.42 (2 H, br s, =CH_2), 7.13 (2 H, dd, *J* 8.9, 1.5, 2 ArH) and 7.28–7.48 (3 H, m, 3 ArH); *m/z* 350 (M^+), 336 (16), 335 (100), 334 (32), 172 (21), 101 (19) and 56 (27).

4,5,5,6,7,7-*Hexamethyl*-8-*methylene*-2-*phenyl*-4β,5,6,7,8,8a-*hexahydrobenzo*[1,2-c:4,5-c′]*dipyrrole*-1,3(2H,3aαH)-*dione* **8j**. Purified by PLC on silica gel (hexane–acetone 45:55). Pale yellow solid, m.p. 85–86 °C (Found: C, 75.8; H, 7.65; N, 7.6. $C_{23}H_{28}N_2O_2$ requires C, 75.82; H, 7.69; N, 7.69%); ν_{max}(KBr)/cm^{-1} 2980, 2940, 2880, 1780, 1715, 1600, 1500, 1390, 1180, 900, 755 and 700; δ_H(200 MHz; $CDCl_3$) 1.05, 1.07, 1.18 and 1.33 (12 H, 4 s, 4 × Me), 1.23 (3 H, d, *J* 7.2, Me), 2.28 (3 H, s, NMe), 3.15 (1 H, dq, *J* 1.6, 7.2, C*H*Me), 3.20 (1 H, dd, *J* 8.4, 1.6, CHCO), 3.65 (1 H, dd, *J* 8.4, 1.0, CHC=), 5.39 (1 H, br d, *J* 1.0, =CH), 5.42 (1 H, s, =CH) and 7.12–7.45 (5 H, m, Ph); *m/z* 364 (M^+ absent), 349 (24), 335 (100), 172 (18), 107 (19), 101 (28) and 56 (18).

Ethyl syn-4-*ethyl*-7-*ethylidene*-1,1,2,3,3-*pentamethyl*-2,3,4α,5α,6,7-*hexahydro*-1H-*isoindole*-5-*carboxylate* **8k**. Two isomers were isolated by PLC on silica gel (hexane–acetone 75:25). Fastest moving band gave a pale yellow oil, b.p. 145 °C (10 Pa) (Found: C, 75.2; H, 10.3; N, 4.3. $C_{20}H_{33}NO_2$ requires C, 75.24; H, 10.34; N, 4.39%); ν_{max}(film)/cm^{-1} 2980, 2945, 1740, 1475, 1380, 1280, 1175, 1050, 900 and 825; δ_H(400 MHz; $CDCl_3$) 0.83 (3 H, t, *J* 7.3, Me), 1.15 (6 H, s, 2 × Me), 1.20 and 1.38 (6 H, 2 s, 2 × Me), 1.24 (3 H, t, *J* 7.1, Me), 1.49 (1 H, dq, *J* 14.4, 7.3, C*H*HMe), 1.63 (1 H, ddq, *J* 14.4, 5.8 and 7.3, CH*H*Me), 1.79 (3 H, dd, *J* 7.4, 1.2, =CMe), 2.24 (1 H, br dd, *J* 13.0, 10.8, C=CC*H*H), 2.29 (3 H, s, NMe), 2.44 (1 H, br dd, *J* 13.0, 4.3, C=CCH*H*), 2.62 (1 H, ddd, *J* 10.8, 4.3 and 5.8, C*H*CO_2Et), 2.63–2.78 (1 H, m, C*H*Et; after decoupling from CH_2Me, d, *J* 5.8), 4.12 and 4.13 (2 H, 2 q, *J* 7.1, OC*H*$_2$Me) and 5.40 (1 H, br q, *J* 7.4, =C*H*Me); δ_C(100 MHz; $CDCl_3$; quaternary carbons are omitted) 9.84 (1 C, *Me*CH_2CH), 14.26 (1 C, *Me*CH_2O), 17.18 (1 C, *Me*C=), 24.76 (2 C, 2 × Me), 24.78 (1 C, Me), 25.74 (1 C, Me), 26.18 (1 C, MeCH_2CH), 26.46 (1 C, NMe), 37.52 (1 C, *C*HEt), 40.54 (1 C, *C*H_2C=), 45.65 (1 C, *C*HCO), 60.36 (1 C, OCH_2) and 119.11 (1 C, =*C*HMe); *m/z* 319 (M^+), 305 (100), 304 (19), 246 (16), 216 (16), 201 (18), 186 (17), 177 (22), 172 (28), 162 (23) and 56 (33).

Second fastest moving isomer, anti-**8k**, was a pale yellow oil b.p. 139 °C (10 Pa) (Found: C, 75.2; H, 10.3; N, 4.3%); ν_{max}(film)/cm^{-1} 2980, 2895, 1745, 1470, 1375, 1295, 1170, 1030, 920 and 835; δ_H(400 MHz; $CDCl_3$) 0.86 (3 H, t, *J* 7.3, 4-CH_2*Me*), 1.14, 1.20, 1.23 and 1.38 (12 H, 4 s, 4 × Me), 1.28 (3 H, t, *J* 7.3, OCH_2*Me*), 1.44–1.73 (2 H, m, 4-C*H*$_2$Me), 1.86 (3 H, d pseudo t, *J* 7.6, 1.3 and 1.4, =CMe), 2.31 (3 H, s, NMe), 2.44 (1 H, br dd, *J* 14.2, 4.9, MeC=CC*H*H), 2.52–2.60 (2 H, group of m, C*H*CO_2Et, C*H*Et; after decoupling from CH_2Me, 2.53–2.57, m, C*H*CO_2Et; 2.58, d, *J* 5.0, C*H*Et), 2.83 (1 H, dddq, *J* 14.2, 11.2, 1.8 and 1.4, MeC=CCH*H*), 4.13 and 4.16 (2 H, q system, *J* 7.1, OC*H*$_2$Me) and 5.38 (1 H, q pseudo t, *J* 7.6, 1.8, 1.4, =C*H*Me); δ_C(100 MHz; $CDCl_3$; quaternary carbons are omitted) 13.56 (1 C, *Me*CH_2CH), 14.26 (1 C, *Me*CH_2O), 17.72 (1 C, *Me*C=), 23.10 (1 C, CH*C*H_2Me), 24.57 (2 C, 2 × Me), 25.21 (1 C, Me), 26.45 (1 C, Me), 26.48 (1 C, NMe), 34.69 (1 C, *C*H_2C=), 38.00 (1 C, *C*HEt), 44.77 (1 C, *C*HCO), 61.87 (1 C, OCH_2) and 120.06 (1 C, =*C*HMe); *m/z* 319 (M^+ absent), 306 (21), 305 (100), 260 (15), 246 (16), 202 (16), 176 (24), 162 (22) and 56 (35).

Diethyl syn-4-*ethyl*-7-*ethylidene*-1,1,2,3,3-*pentamethyl*-2,3,4α,5α,6β,7-*hexahydro*-1H-*isoindole*-5,6-*dicarboxylate* **8l**. Two isomers were isolated by PLC on silica gel (hexane–acetone 70:30). The *major isomer* (fastest moving band) was a pale yellow oil, b.p. 153 °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%); ν_{max}(film)/cm^{-1} 2980, 2940, 1745, 1735, 1470, 1380, 1290, 1170, 1040, 940 and 870; δ_H(400 MHz; $CDCl_3$) 0.83 (3 H, t, *J* 7.5, Me), 1.02, 1.08, 1.13 and 1.31 (12 H, 4 s, 4 × Me), 1.19 and 1.24 (6 H, 2 t, *J* 7.0, 2 × OCH_2*Me*), 1.48 (1 H, dq, *J* 14.3, 7.5, C*H*HMe), 1.65 (1 H, ddq, *J* 14.3, 7.5 and 3.8, CH*H*Me), 1.69 (3 H, dd, *J* 7.2, 1.6, =CMe), 2.32 (3 H, s, NMe), 2.46–2.56 (1 H, m, C*H*Et; after decoupling from CH_2, d, *J* 4.9), 2.99 (1 H, dd, *J* 10.6, 4.9, C*H*CO_2Et), 3.20 (1 H, d pseudo quintet, *J* 10.6, =CC*H*CO_2Et), 4.10 and 4.15 (4 H, 2 q, *J* 7.0, 2 × CH_2) and 5.18 (1 H, qd, *J* 7.2, 1.6, =C*H*Me); *m/z* 391 (M^+ absent), 377 (20), 376 (100), 302 (15), 200 (18) and 56 (22).

anti-4α,5α,6β-*Isomer* **8l** (second fastest moving band), pale yellow oil, b.p. 146 °C (7 Pa) (Found: C, 70.5; H, 9.4; N, 3.5%); ν_{max}(film)/cm^{-1} 2980, 2940, 2800, 1745, 1740, 1380, 1290, 1170, 1040, 940 and 870; δ_H(400 MHz; $CDCl_3$) 0.78 (3 H, t, *J* 7.3, Me), 0.92, 1.11, 1.14 and 1.31 (12 H, 4 s, 4 × Me), 1.17 and 1.24 (6 H, 2 t, *J* 7.0, 2 × OCH_2*Me*), 1.58–1.73 (2 H, 2 m, C*H*$_2$Me), 1.74 (3 H, dd, *J* 7.1, 0.7, Me), 2.34 (3 H, s, NMe), 2.57–2.70 (1 H, m, C*H*Et; after decoupling, d, *J* 4.5), 2.96 (1 H, dd, *J* 4.5, 8.9, C*H*CO_2Et), 3.87 (1 H, br d, *J* 8.9, =CC*H*CO_2Et), 4.40–4.15 (4 H, system of 2 q, *J* 7.0, OCH_2Me) and 5.80 (1 H, dq, *J* 0.7, 7.1, =C*H*Me); *m/z* 390 (M^+ − 1), 377 (18), 376 (100), 302 (21), 200 (18) and 56 (28).

Methyl syn-4-*ethyl*-7-*ethylidene*-1,1,2,3,3,6-*hexamethyl*-2,3,4α,5α,6β,7-*hexahydro*-1H-*isoindole*-5-*carboxylate* **8m**. Two isomers were isolated by PLC on silica gel (hexane–acetone 70:30).

The *major one* (fastest moving band) was an oil, b.p. 151 °C (8 Pa) (Found: C, 75.15; H, 10.3; N, 4.3. $C_{20}H_{33}NO_2$ requires C, 75.24; H, 10.34; N, 4.39%); ν_{max}(film)/cm^{-1} 2980, 2940, 1745, 1470, 1365, 1265, 1170, 1105, 1030 and 810; δ_H(400 MHz; $CDCl_3$) 0.82 (3 H, t, *J* 7.0, CH_2*Me*), 1.05 (3 H, d, *J* 6.4, CH*Me*), 1.06, 1.11, 1.18 and 1.36 (12 H, 4 s, 4 × Me), 1.38–1.49 (1 H, m, C*H*HMe), 1.48–1.56 (1 H, m, CH*H*Me), 1.75 (3 H, dd, *J* 7.0, 1.5, =CMe), 2.13 (1 H, dd, *J* 10.7, 5.2, CHCO), 2.27 (1 H, m, C*H*Me; after decoupling from Me, d, *J* 10.7), 2.30 (3 H, s, NMe), 2.48–2.54 (1 H, m, C*H*Et; after decoupling from CH_2, d, *J* 5.2), 3.70 (3 H, s, OMe) and 5.37 (1 H, q, *J* 7.0, =C*H*Me); *m*/*z* 319 (M^+), 305 (78), 304 (100), 260 (23), 244 (21), 216 (24), 200 (22), 191 (44), 185 (23), 162 (24), 123 (36) and 56 (88).

anti-*Isomer of* **8m** was the second fastest isomer, an oil, b.p. 147 °C (8 Pa) (Found: C, 75.15; H, 10.3; N, 4.3%); ν_{max}(film)/cm^{-1} 2980, 2940, 1745, 1475, 1370, 1270, 1170, 1105, 1025 and 810; δ_H(400 MHz; $CDCl_3$) 0.80 (3 H, t, *J* 7.0, CH_2*Me*), 1.01 (3 H, d, *J* 6.9, CH*Me*), 1.09, 1.15, 1.19 and 1.39 (12 H, 4 s, 4 × Me), 1.49–1.57 (2 H, m, CH_2Me), 1.76 (3 H, d, *J* 7.0, =CMe), 2.10 (1 H, dd, *J* 8.1, 4.5, C*H*CO), 2.32 (3 H, s, NMe), 2.56–2.59 (1 H, m, C*H*Et; after decoupling from CH_2, d, *J* 4.5), 3.07 (1 H, dq, *J* 8.1, 6.9, C*H*Me), 3.74 (3 H, s, OMe) and 5.48 (1 H, q, *J* 7.0, =C*H*Me); *m*/*z* 319 (M^+), 305 (77), 304 (100), 260 (24), 216 (18), 200 (17), 191 (36), 185 (19), 162 (18), 123 (19) and 56 (22).

Isomers of compound **14** (ethyl 7-methyl-10-methylene-7,8,9,10-tetrahydrofluoranthene-8-carboxylate) could not be separated and the product was isolated as the fully aromatic system **13** (reported in the preceding paper).

1,1,2,3,3,4-*Hexamethyl*-6,7-*dimethylene*-2,3,4,5,6,7-*hexahydro*-1H-*isoindole*-5-*spiro*-3′-(4′-*ethylidene*-2′,3′,4′,5′-*tetrahydro*-1′,2′,2′,5′,5′-*pentamethylpyrrole*) **15**. Isolated by PLC on silica gel (hexane–acetone 80:20). Pale yellow oil, b.p. 167 °C (7 Pa) (Found: C, 81.6; H, 10.9; N, 7.3. $C_{26}H_{42}N_2$ requires C, 81.68; H, 10.99; N, 7.33%); ν_{max}(film)/cm^{-1} 2980, 2940, 2800, 1660, 1645, 1460, 1375, 1180, 890 and 830; δ_H(200 MHz; $CDCl_3$) 1.09, 1.19 and 1.22 (9 H, 3 s, 3 × Me), 1.27 and 1.31 (12 H, 2 s, 4 × Me), 1.34 (3 H, d, *J* 7.6, Me), 1.42 (3 H, s, Me), 1.86 (3 H, d, *J* 7.4, Me), 2.14 and 2.29 (6 H, 2 s, 2 × NMe), 2.70 (1 H, q, *J* 7.6, C*H*Me), 4.97 (1 H, br s, =CH), 5.01 (1 H, s, =CH), 5.18 (1 H, s, =CH), 5.32 (1 H, q, *J* 7.4, =C*H*Me) and 5.37 (1 H, s, =CH); *m*/*z* 383 (M^+ + 1), 382 (M^+ 23), 368 (53), 367 (100), 296 (12) and 176 (12).

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