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Solvent-free synthesis of 4,4-bis-functionalized-1,6-dienes and 1,6-diynes on the surface of neutral alumina

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Dedicated to Professor U. R. Ghatak on the occasion of his 70th birthday

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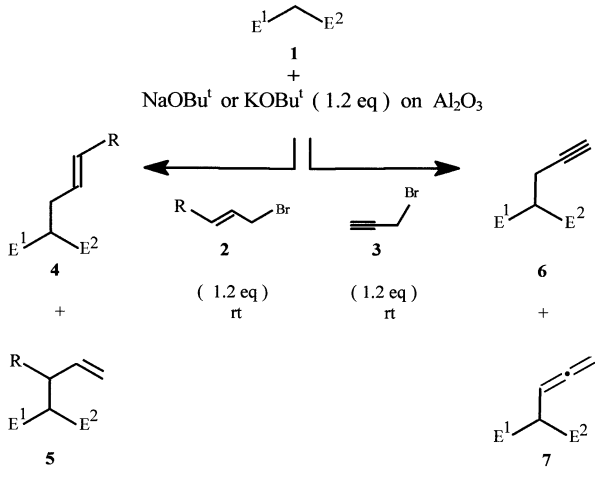
Abstract—An improved procedure has been developed for the synthesis of structurally varied 4,4-bis-functionalized-1,6-dienes and 1,6-diynes through regioselective alkylation of active methylene compounds with several unsymmetrical allyl bromides and propargyl bromide on the surface of neutral alumina impregnated with sodium ethoxide or potassium *tert*-butoxide in the absence of any solvent under environmentally benign conditions.

1. Introduction

4,4-bis-Functionalized-1,6-dienes and 1,6-diynes find immense applications for the construction of structurally varied carbocycles via ring closing metathesis,[1] Pauson–Khand reaction[2] and Pd-catalyzed cyclization/hydrosilylation[3] protocols. The said compounds are commonly prepared by diallylation of active methylene compounds with allyl halides and propargyl halides under basic conditions which are often complicated because of concomitant O-alkylation, Claisen retrogression of 1,3-dicarbonyl compounds and allylic rearrangement of propargyl and unsymmetrical allyl halides.[4] Although very recently, during the synthesis of angularly fused tricyclic systems via tandem ring closing metathesis reaction, DBU-mediated zero-valent palladium-catalyzed allylation of 1,3-dicarbonyl compounds has been reported,[1d] there is still a need for a simple, cost-effective and more general method for the regioselective C-dialkylation of active methylene compounds with propargyl and unsymmetrical allyl halides.

The art of performing efficient chemical transformation in a single operation by reusable catalyst avoiding toxic and costly reagents, large amounts of solvents and expensive purification techniques, represents a fundamental target of the modern organic synthesis.[5] Reactions using reagents and/or reactants on insoluble inorganic support in absence of any solvent have stimulated considerable interest among synthetic chemists worldwide.[6] Advantages frequently claimed in favour of supported reagents compared with their homogeneous counterparts are ease of set-up and work-up, mild experimental conditions, rapid reactions and gain in yield and/or selectivity. Quite a few years ago, reports of surface-mediated Michael reactions and highly selective C-alkylation of 1,3-dicarbonyl compounds have come out in the literature.[7] As a part of our endeavour to develop highly selective, operationally simple, economically viable and environmentally benign methodology for important synthetic transformations[8] we report herein a regioselective diallylation and dipropargylation of active methylene compounds in dry medium on the surface of neutral alumina impregnated with sodium or potassium alkoxide to generate functionally varied 4,4-disubstituted 1,6-dienes and 1,6-diynes.



Scheme 1.

Keywords: regiocontrol; solid-phase synthesis; supported reagents; dienes and diynes.

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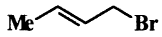
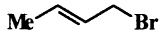
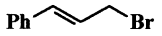
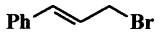
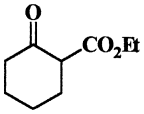
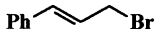
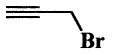
Table 1. Monoalkylation of active methylene compounds with unsymmetrical allyl bromides and propargyl bromide

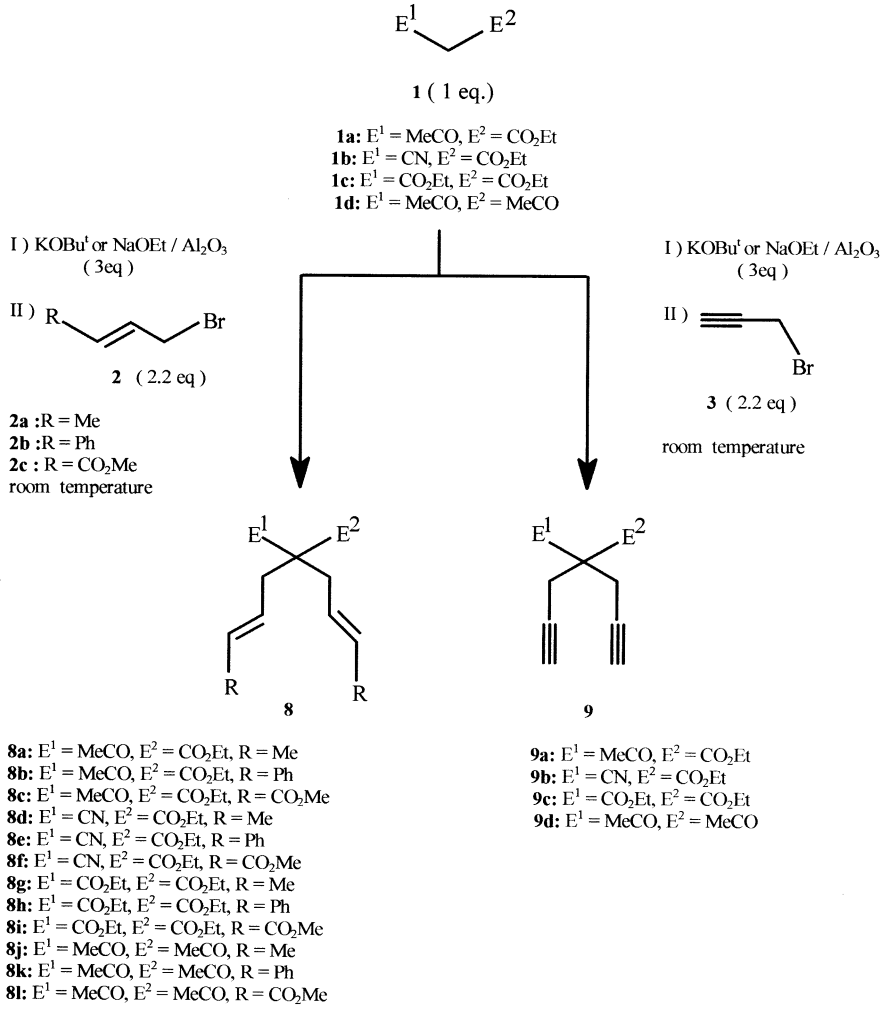
Entry no.	Active methylene compound (**1**) E^1	E^2	Alkyl halide **2/3**	Time (h)	Yield (%) of **4/6**	Yield (%)[a] of **5/7**
1	MeCO	CO_2Et		1	70[a]	–
2	CO_2Et	CO_2Et		1	68[a]	–
3	MeCO	CO_2Et		2	75[b]	–
4	CO_2Et	CO_2Et		2	67[a]	–
5				4	78[b]	–
6	MeCO	CO_2Et		1	77[a]	–

[a] % by ^1H NMR, remainder starting material.
[b] Isolated pure product.

2. Results and discussion

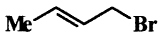
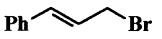
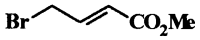
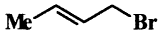
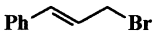
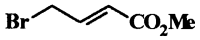
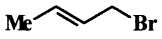
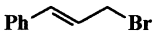
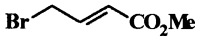
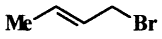
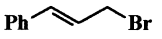
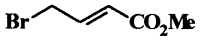
At the outset, to check the feasibility of the surface-mediated alkylation technique with propargyl and unsymmetrically substituted allyl bromides, the following mono-alkylation study was undertaken (Scheme 1), results of which has been furnished in Table 1.

As shown in Table 1, different 1,3-dicarbonyl compounds (**1**) underwent highly regioselective mono-C-alkylation with structurally varied unsymmetrical allyl bromides (**2**) and propargyl bromide (**3**) at room temperature in good yield and purity within a reasonably short period of time, even when both the substrate and the allyl halide are sterically congested (Table 1, entry 5). The most important



Scheme 2.

Table 2. Diallylation and dipropargylation of active methylene compounds

Entry No.	E^1	E^2	Alkyl halide	Time (h)	Yield (%)[a]
1	MeCO	CO_2Et		1	81
2	MeCO	CO_2Et		3	80
3[b]	MeCO	CO_2Et		2	69
4	MeCO	CO_2Et		1.5	85
5	CN	CO_2Et		1	80
6	CN	CO_2Et		3	78
7[b]	CN	CO_2Et		2	80
8	CN	CO_2Et		1	84
9	CO_2Et	CO_2Et		1.5	79
10	CO_2Et	CO_2Et		3	76
11[b]	CO_2Et	CO_2Et		3.5	82
12	CO_2Et	CO_2Et		2.5	85
13	MeCO	MeCO		2	80
14	MeCO	MeCO		3	75
15[b]	MeCO	MeCO		2	78
16	MeCO	MeCO		1	71

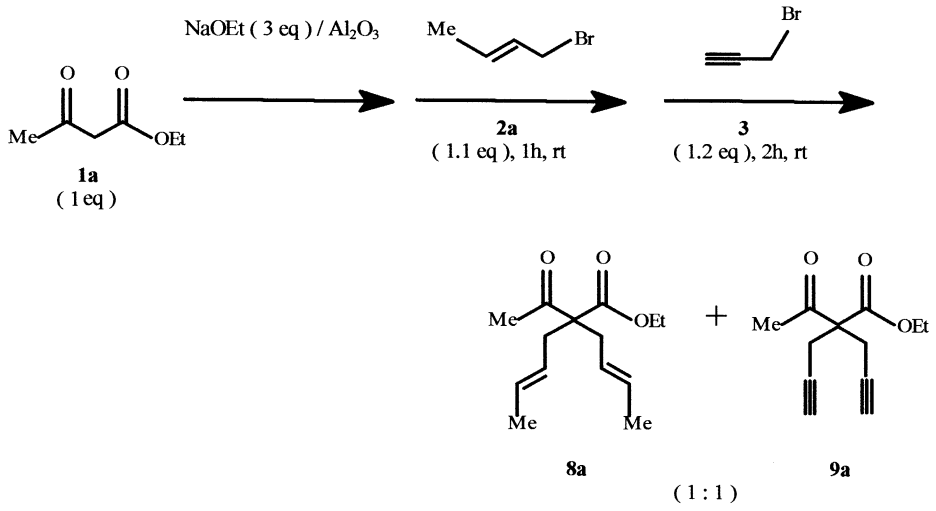
[a] Yield refers to isolated product purified by column chromatography or short-path distillation and fully characterized by IR and ^{1}H NMR spectroscopy.
[b] KOBu^t was used instead of NaOEt to obtain better results.

feature of the present method seems to be the negligible formation of any product (maximum 2%) (**5** or **7**) arising from allylic rearrangement in each case. Use of NaOEt in place of NaOBu^t or KOBu^t led to the formation of considerable amount of di-C-alkylated products along with monoalkylated ones.

Inspired by the above results, attempts were made to synthesize a series of structurally different 4,4-bis-functionalized 1,6-dienes and 1,6-diynes by base-promoted surface-mediated regioselective dialkylation of active methylene compounds (**1a**–**1d**) with unsymmetrically substituted allyl bromides (**2a**–**2c**) and propargyl bromide (**3**) on the surface of neutral alumina impregnated with NaOEt or KOBu^t in absence of any solvent, as shown in Scheme 2. The results are shown in Table 2.

As evident from Table 2, several substituted 1,6-dienes (**8a**–**8l**) and 1,6-diynes (**9a**–**9d**) have been synthesized by the present method in good yield, high purity and with excellent selectivity within the reasonable period of time using easily available non-toxic materials. No Claisen retrogression of the products (a very common side reaction[9] for non-enolizable 1,3-diketones, β-ketoesters and 1,3-diesters) was observed in spite of the presence of excess nucleophilic base (ethoxide). Negligible occurrence of allylic rearrangement in the propargyl and allyl moieties (not more than 2% as evident from ^{1}H NMR studies) is manifested in the high regioselectivity of the said process. The stereochemistry of the double bond in the halide has also been found unaltered in the product (as evident from the coupling constants of the olefinic protons in ^{1}H NMR spectra). Better yields are obtained using potassium *tert*-butoxide as base instead of sodium ethoxide for methyl γ-bromocrotonate, presumably due to concomitant transesterification and nucleophilic addition by ethoxide, which is not very pronounced with the relatively less nucleophilic base *tert*-butoxide. The products are purified by column chromatography over neutral alumina or short path distillation. 1,6-Diynes having various functionalities at C_4-position prepared by this method find immense applications in various useful cyclopolymerisation reactions.[10] This methodology can therefore be applied for the synthesis of various 1,6-dienes and 1,6-diynes having requisite substituents at 1- and 6-position with the potential for constructing important substituted carbocycles and spiro compounds related to important natural product skeletons by suitable modification and elaboration of various functionalities located at 4-position.

The present surface-mediated reactions in solvent-free medium have been found to be more effective and efficient than those in solution in terms of rate, yield and purity. The said reactions are slower in solution than in dry state adsorption condition (DSAC). Reaction between ethyl acetoacetate and cinnamyl bromide in anhydrous dichloromethane in the presence of neutral alumina impregnated with sodium ethoxide for 3 h led to the formation of a mixture of 57% mono- and 43% dialkylated product (as indicated by ^{1}H NMR studies), whereas the same reaction in DSAC leads to exclusive dialkylation (entry 2 in Table 2). Ethyl acetoacetate reacts with propargyl bromide in presence of sodium ethoxide in ethanol in absence of alumina, but the product is obtained in much lower yield (~55%) and considerable amount of side products are



Scheme 3.

formed, which decreases the purity of the alkylated product to great extent. Sodium ethoxide in ethanol has been found to be detrimental; with cinnamyl bromide and methyl γ-bromocrotonate, extensive polymerization of the double bond occurs with very little alkylation of active methylene compound. Clearly the basicity of ethoxide when impregnated with alumina is so attenuated that it is sufficient to deprotonate the active methylenes but insufficient to promote base-catalyzed polymerization of allyl halides making the DSAC-methods more attractive than the conventional ones. Stirring for 1 h after addition of crotyl bromide (1.1 equiv.) to ethyl acetoacetate (1 equiv.) adsorbed on alumina impregnated with NaOEt (3 equiv.) followed by the addition of propargyl bromide (1.2 equiv.) in the same pot and stirring for further 2 h led to the formation of dicrotyl (**8a**) and dipropargyl (**9a**) adducts, no trace of crotyl-propargyl product was detected (Scheme 3).

3. Conclusions

The present surface-mediated solid-phase procedure on the surface of neutral alumina provides an efficient methodology for the synthesis of a variety of 4,4-bis-functionalized 1,6-disubstituted dienes and 1,6-diynes from easily accessible starting materials. The notable advantages of the present procedure include (a) good yield (70–85%), (b) reasonably rapid reactions (1–3 h), (c) mild reaction conditions, (d) ease of set-up and work-up, (e) use of relatively non-toxic reagents and solvents and (f) general applicability accommodating a variety of substitution patterns. Alumina recovered after the reaction can be recycled after washing with methanol and activation with little variation of yield. Therefore, this allylation approach has set out to minimize the use of offensive materials and maximize the use of renewable resources. For these reasons it can be considered as a relatively green technology.

Essential features of this methodology are

(a) no O-allylation and Claisen retrogression of non-enolizable 1,3-dicarbonyl compounds;
(b) no allylic rearrangement of the unsymmetrical allyl bromides and propargyl bromide;
(c) preservation of stereochemistry of the olefinic linkages;
(d) decreased polymerization of certain allyl halides, especially cinnamyl bromide and methyl γ-bromocrotonate under basic condition;
(e) reactions in DSAC are faster than in solution;
(f) good yield of the products obtained under relatively mild conditions by an economically viable and environmentally friendly method.

Further investigations on the mechanistic aspects of this reaction and its applications in organic synthesis are currently underway.

4. Experimental

General: ^{1}H NMR spectra were recorded at 60 MHz on EM 360 spectrometer of Varian Associates in CCl_4 solutions and at 300 MHz on Bruker-300 spectrometer in $CDCl_3$ solutions using Me_4Si as internal standard. IR spectra were recorded on Perkin Elmer 298 spectrometer in $CHCl_3$ solution. Elemental analyses were performed on Perkin Elmer C, H, N Autoanalyser. Alumina, supplied by SRL, India (Aluminium oxide, neutral, Brockmann activity, grade 1 for column chromatography) was used in all the reactions. The allyl and propargyl halides were prepared following standard procedures. All the chemicals were distilled before use.

4.1. General procedure for the solvent-free synthesis of 4,4-bis-functionalized 1,6-dienes (8a–8l) and 1,6-diynes (9a–9d)

To a solution of sodium ethoxide in dry ethanol (or potassium *tert*-butoxide in dry *tert*-butanol as the case may be) (15 mmol), neutral alumina (15 times the weight of the active methylene sustrate, activated by heating at 180°C under vacuum for 2 h followed by cooling and storage under argon) was added with stirring followed by

evaporation of the solvent under reduced pressure to obtain an easy flowing powder. The substrate (5 mmol) was added dropwise to the supported reagent under nitrogen with vigorous stirring. Stirring was continued for 10 min at room temperature. Then the reaction mixture was cooled in ice and the alkyl halide (11 mmol) was added dropwise under stirring condition. The reaction mixture was then allowed to attain room temperature and left at room temperature with intermittent stirring (to ensure complete mixing) till completion of the reaction (monitored with TLC). The product was extracted from the solid mass by filtration chromatography over a short plug of neutral alumina using dichloromethane as solvent. Evaporation of solvent under reduced pressure furnished the crude product, which was further purified by column chromatography over neutral alumina or short path distillation.

For solid alkyl halide (cinnamyl bromide), ethereal solution was added to the reaction mixture at 0°C followed by evaporation of the solvent under reduced pressure and left at room temperature till the completion of the reaction. Reactions on a gram scale also furnished analogously good yield.

The products were easily identified by their spectral (IR and ^{1}H NMR) data which are presented here for ready reference.

4.1.1. Ethyl 2,2-bis-(but-2-enyl)-3-oxo-butanoate (8a).[1a] Colourless oil; purified by column chromatography on neutral alumina (3% EtOAc/petroleum ether); yield 81%; IR: 1710 cm^{-1} (s), 1740 cm^{-1} (s); ^{1}H NMR (60 MHz, CCl_4); δ 1.20 (3H, t, J=7 Hz, –OCH$_2$C*H*$_3$); 1.58 (6H, d, J=6 Hz, C*H*$_3$CH=); 1.95(3H, s, C*H*$_3$CO–);2.36 (4H, d, J=7 Hz, –C*H*$_2$CH=); 4.06 (2H, q, J=7 Hz, –OC*H*$_2$CH$_3$); 4.77–5.67 (4H, m., –C*H*=C*H*–).

4.1.2. Ethyl 3-oxo-2,2-bis-(-3-phenylprop-2-enyl)-butanoate (8b). Colourless highly viscous oil; purified by column chromatography on neutral alumina (3% EtOAc/petroleum ether); yield 80%; IR: 1710 cm^{-1} (s), 1740 cm^{-1} (s); ^{1}H NMR (60 MHz, CCl_4); δ 1.16 (3H, t, J=7 Hz, –OCH$_2$C*H*$_3$); 2.06 (3H, s, C*H*$_3$CO–); 2.71(4H, d, J=6 Hz, C*H*$_2$CH=); 4.15(2H, q, J=7 Hz, –OC*H*$_2$CH$_3$); 5.93 (2H, td, J_1=16 Hz, J_2=6 Hz, –C*H*=CHPh); 6.39 (2H, d, J=16 Hz, –CH=C*H*Ph); 7.26 (10H, br. s., Aromatic-H); Anal. Found C, 79.34; H, 7.25. $C_{24}H_{26}O_3$ requires C, 79.55; H, 7.18.

4.1.3. Dimethyl 5-ketomethyl-5-ethoxycarbonylnona-2,7-diene-1,9-dioate (8c). Colourless oil; distilled at 155°C at 0.04 mm of Hg, yield 69%; IR: 1710 cm^{-1} (s), 1740 cm^{-1} (s) ^{1}H NMR (60 MHz, CCl_4): δ 1.29 (3H, t, J=7 Hz, –OCH$_2$C*H*$_3$); 2.16 (3H, s, C*H*$_3$CO); 2.73 (4H, d, J=8 Hz, –C*H*$_2$CH=); 3.66 (6H, s, –COOC*H*$_3$); 4.28 (2H, q, J=7 Hz, –OC*H*$_2$CH$_3$); 5.86 (2H, d, J=16 Hz, =C*H*COOCH$_3$); 6.17–6.99 (2H, m, –C*H*=CHCOOCH$_3$) Anal. Found C, 58.61; H, 6.98. $C_{16}H_{22}O_7$ requires C, 58.89; H, 6.75.

4.1.4. Ethyl 2-cyano-2-(but-2-enyl)-hex-4-ene-1-oate (8d).[1b] Colourless viscous oil; purified by column chromatography on neutral alumina (7% EtOAc/petroleum ether), yield 80%; IR: 1730 cm^{-1} (s), 2240 cm^{-1} (vw); ^{1}H NMR (60 MHz, CCl_4): δ 1.18 (3H, t, J=7 Hz, –OCH$_2$C*H*$_3$); 1.28 (6H, d, J=4 Hz, =CHC*H*$_3$); 2.32 (4H, d, J=5 Hz, –C*H*$_2$CH=); 4.12 (2H, q, J=7 Hz, –OC*H*$_2$CH$_3$); 4.99–5.87 (4H, m, –C*H*=C*H*–).

4.1.5. Ethyl 2-cyano-2-(3-phenylprop-2-enyl)-5-phenyl-pent-4-ene-1-oate (8e). Colourless viscous oil; purified by column chromatography on neutral alumina (7% EtOAc/petroleum ether), yield 78%; IR: 1730 cm^{-1} (s), 2240 cm^{-1} (vw); ^{1}H-NMR (60 MHz, CCl_4): δ 1.49 (3H, t, J=7 Hz, –OCH$_2$C*H*$_3$); 3.02 (4H, d, J=7 Hz, –C*H*$_2$CH=); 4.49 (2H, q, J=7 Hz, –OC*H*$_2$CH$_3$); 6.20–6.73 (2H, m, –C*H*=CHPh); 6.88 (2H, d, J=16 Hz; –CH=C*H*Ph); 7.57 (10H, br.s, Aromatic – H). Anal. Found C, 80.29; H, 6.39; N, 4.23. $C_{23}H_{23}O_2N$ requires C, 80.01; H, 6.66; N, 4.05.

4.1.6. Dimethyl 5-cyano-5-ethoxycarbonylnona-2,7-diene-1,9-dioate (8f). Colourlerss oil; distilled at 160°C at 0.03 mm of Hg, yield 80%; IR: 1715 cm^{-1} (s), 1740 cm^{-1} (s); 2240 cm^{-1} (vw); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32 (3H, t, J=7 Hz; –OCH$_2$C*H*$_3$); 2.58–2.95 (4H, m, –CH$_2$CH=); 3.75 (6H, s, –COOCH$_3$); 4.30 (2H, q, J=7 Hz, –OC*H*$_2$CH$_3$); 6.00 (2H, d, J=15.5 Hz, –CH=C*H*COOCH$_3$); 6.86 (2H, td, J_1=15.5 Hz, J_2=7.6 Hz, –C*H*=CHCOOCH$_3$) Anal. Found C, 57.98; H, 5.90; N, 4.28. $C_{15}H_{19}O_6N$ requires C, 58.25; H, 6.15; N, 4.53.

4.1.7. Diethyl 2,2-bis-(but-2-enyl)-propane-1,3-dioate (8g).[1a,c] Colourless oil; purified by column chromatography on neutral alumina (3% EtOAc/petroleum ether), yield 79%; IR: 1725 cm^{-1} (s); ^{1}H-NMR (60 MHz, CCl_4): δ 1.23 (6H, t, J=7 Hz, –OCH$_2$C*H*$_3$); 1.64 (6H, d, J=6 Hz, C*H*$_3$CH=) 2.43 (4H, d, J=6 Hz, –C*H*$_2$CH=); 4.12 (4H, q, J=7 Hz; –OC*H*$_2$CH$_3$); 4.93–5.69 (4H, m, –C*H*=C*H*–).

4.1.8. Diethyl 2,2-bis-(3-phenylprop-2-enyl)-propane-1,3-dioate (8h). Colourless oil; purified by column chromatography on neutral alumina (5% EtOAc/petroleum ether), yield 76%; IR: 1725 cm^{-1} (s); ^{1}H NMR (60 MHz, CCl_4): δ 1.40 (6H, t, J=7 Hz, –OCH$_2$C*H*$_3$); 2.96 (4H, d, J=7 Hz; –C*H*$_2$CH=); 4.36 (4H, q, J=7 Hz, –OC*H*$_2$CH$_3$); 5.97–6.53 (2H, m, –C*H*=CHPh); 6.70 (2H, d, J=16 Hz, –CH=C*H*Ph); 7.47 (10H, br.s, Aromatic-H). Anal. Found C, 76.34; H, 7.27. $C_{25}H_{28}O_4$ requires C, 76.53; H, 7.14.

4.1.9. Dimethyl 5,5-bis-(ethoxycarbonyl)-nonane-2,7-diene-1,9-dioate (8i). Colourless oil; distilled at 160°C at 0.06 mm of Hg, yield 82%; IR, 1715 cm^{-1}(s), 1740 cm^{-1}(s); ^{1}H NMR (300 MHz, $CDCl_3$), δ 1.26 (6H, t, J=7 Hz, –OCH$_2$C*H*$_3$); 2.78 (4H, d, J=7.5 Hz, –C*H*$_2$CH=); 3.73 (6H, s, COOC*H*$_3$); 4.22 (4H, q, J=7 Hz, –OC*H*$_2$CH$_3$); 5.89 (2H, d, J=15.5 Hz, –CH=C*H*COOCH$_3$); 6.78 (2H, td J_1=15.5 Hz, J_2=7.5 Hz, –C*H*–CHCOOCH$_3$) Anal. Found C, 57.42; H, 6.79. $C_{17}H_{24}O_8$ requires C, 57.30; H 6.74.

4.1.10. 3,3-bis-(But-2-enyl)-pentane-2,4-dione(8j).[1b] Colourless oil; purified by column chromatography on neutral alumina (5% EtOAc/petroleum ether) yield 80%; IR: 1700 cm^{-1}(s); ^{1}H NMR (60 MHz, CCl_4): δ 1.68 (6H, d, J=6 Hz, –CH$_3$); 2.03 (6H, s, C*H*$_3$CO–), 2.53 (4H, d, J=8 Hz, –CH$_2$); 4.87–5.87 (4H, m, –C*H*=C*H*–).

4.1.11. 3,3-bis-(3-Phenylprop-2-enyl)-pentane-2,4-dione (8k). Colourless highly viscous oil; distilled at 165°C at 0.03 mm of Hg, yield 75%; IR: 1710 cm^{-1}(s); ^1H NMR (60 MHz, CCl_4): δ 2.17(6H, s, CH_3CO–); 2.83 (4H, d, J=8 Hz, –CH_2CH=); 5.63–6.37 (2H, m, –CH=CHPh); 6.49 (2H, d, J=16 Hz, –CH=CHPh); 7.27 (10H, br. s, Aromatic-H). Anal. Found C, 82.91; H, 7.34. $C_{23}H_{24}O_2$ requires C, 83.13; H, 7.23.

4.1.12. Dimethyl 5,5-bis-(ketomethyl)-nonane-2,7-diene-1,9-dioate (8l). White crystalline solid, crystallised from dichloromethane/petroleum ether, yield 78%, mp 126°C; IR: 1700 cm^{-1}(s), 1715 cm^{-1}(s); ^1H NMR (300 MHz, $CDCl_3$): δ 2.14 (6H, s, CH_3CO–); 2.81 (4H, d, J=7.5 Hz, –CH_2CH=); 3.73 (6H, s, –$COOCH_3$); 5.91 (2H, d, J=15.5 Hz, –CH=$CH$$COOCH_3$); 6.61 (2H, td, J_1=15.5 Hz, J_2=7.5 Hz, –CH=$CHCOOCH_3$). Anal. Found C, 60.88; H, 6.81. $C_{15}H_{20}O_6$ requires C, 60.81; H, 6.76.

4.1.13. Ethyl 3-oxo-2,2-bis-(prop-2-ynyl)-butanoate (9a).[10a] Colourless oil, purified by column chromatography on neutral alumina (3% EtOAc/petroleum ether) yield 85%; IR: 1710 cm^{-1}(s), 1740 cm^{-1}(s), 2110 cm^{-1}(vw), 3300 cm^{-1}(s); ^1H NMR (60 MHz, CCl_4): δ 1.27 (3H, t, J=7 Hz, –OCH_2CH_3); 1.92 (2H, t, J=3 Hz, Acetylenic CH); 2.12 (3H, s, CH_3CO–); 2.84 (4H, d, J=3 Hz, –CH_2–); 4.17 (2H, q, J=7 Hz, –OCH_2CH_3).

4.1.14. Ethyl 2-cyano-2-(prop-2-ynyl)-pent-4-yne-1-oate (9b).[10a] Colourless oil, purified by column chromatography on neutral alumina (3% EtOAc/petroleum ether) yield 84%; IR: 1735 cm^{-1}(s), 2100 cm^{-1}(vw); 2240 cm^{-1} (vw); 3300 cm^{-1}(s) ^1H NMR (60 MHz, CCl_4): δ 1.43 (3H, t, J=7 Hz, –OCH_2CH_3); 2.33 (2H, t, J=3 Hz, Acetylenic –CH); 2.97 (4H, d, J=3 Hz, –CH_2–); 4.42 (2H, q, J=7 Hz, –OCH_2CH_3).

4.1.15. Ethyl 2,2-bis-(prop-2-ynyl)-propane-1,3-dioate (9c).[1a,10a,c] Colourless oil, purified by column chromatography on neutral alumina (3% EtOAc/petroleum ether) yield 85%; IR: 1725 cm^{-1}(s), 2110 cm^{-1}(vw), 3300 cm^{-1}(s); ^1H NMR (300 MHz, $CDCl_3$): δ 1.26 (6H, t, J=7 Hz, –OCH_2CH_3); 2.03 (2H, t, J=2.6 Hz, Acetylenic –CH); 2.99 (4H, d, J=2.6 Hz, –CH_2–); 4.23 (4H, q, J=7 Hz, –OCH_2OH_3).

4.1.16. 3,3-bis-(Prop-2-ynyl)-pentane-2,4-dione (9d).[1a,10a] Colourless oil, purified by column chromatography on neutral alumina (5% EtOAc/petroleum ether) yield 71%; IR: 1700 cm^{-1}(s), 2100 cm^{-1}(vw), 3300 cm^{-1}(s); ^1H NMR (300 MHz, $CDCl_3$), δ 2.18 (6H, s, CH_3CO–); 2.56 (2H, t, J=2.5 Hz, Acetylenic –CH); 2.99 (4H, d, J=2.5 Hz, –CH_2–).

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