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From 3,4-dinitrothiophene to 1,2-diaryl-4-nitrobenzenes through (*E*,*E*,*E*)-1,6-diaryl-3-nitro-1,3,5-hexatrienes[☆]

Carlo Dell'Erba,[a,b] Antonella Gabellini,[a] Angelo Mugnoli,[a] Marino Novi,[a,b] Giovanni Petrillo[a,b] and Cinzia Tavani[a,*]

[a]*Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, I-16146 Genova, Italy*
[b]*C.N.R. Centro di Studio per la Chimica dei Composti Cicloalifatici e Aromatici, Via Dodecaneso 31, I-16146 Genova, Italy*

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Abstract—The reactions between 1,2-bis(diethylamino)-2,3-dinitro-1,3-butadiene, easily obtainable by ring-opening of 3,4-dinitrothiophene with diethylamine, and arylmethylmagnesium chlorides in THF at 0°C furnished good yields of (*E*,*E*,*E*)-1,6-diaryl-3-nitro-1,3,5-hexatrienes. To explain the formation of the hexatrienes, a mechanism is advanced which involves, in particular, tautomerisation of the intermediate 1,6-diaryl-3,4-dinitro-2,4-hexadienes followed by base-induced elimination of nitrous acid. The electrocyclic disrotatory conversion of the hexatrienes into the corresponding 5,6-diaryl-2-nitro-1,3-cyclohexadienes was analysed by ^{1}H NMR spectroscopy and exploited for the high-yielding synthesis of 1,2-diaryl-4-nitrobenzenes employing, as oxidants, either DDQ or iodine in the presence of cyclohexene oxide as HI scavenger. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

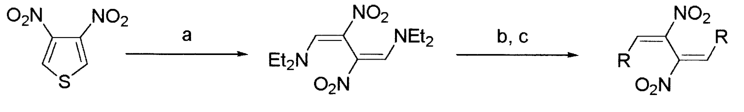
In previous papers[2–4] we have shown that 1,4-bis(diethylamino)-2,3-dinitro-1,3-butadiene **1**, smoothly obtainable via ring-opening of 3,4-dinitrothiophene by action of diethylamine, reacts with alkyl, aryl and vinyl Grignard reagents to furnish good yields of 1,4-dialkyl- (**2a**), 1,4-diaryl-2,3-dinitro-1,3-butadienes (**2b**) and 4,5-dinitro-1,3,5,7-octatetraene derivatives (**2c**), respectively (Scheme 1). Such previously-unknown unsaturated dinitroderivatives, in particular the compounds **2b**, have proved to be interesting building blocks for the synthesis of several and variously functionalised new molecules both in aliphatic and in heterocyclic series.[5,6]

As an extension of a strategy devoted to the exploitation of the parent 3,4-dinitrothiophene as a four-carbon building-block, we have investigated the reactions of compound **1** with some benzylic Grignard reagents. The results reported herein once again show, besides intriguing mechanistic hints, the potential of the above synthetic approach providing a novel route to interesting compounds difficult to prepare by conventional methods.

2. Results and discussion

2.1. Reactions of 1,4-bis(diethylamino)-2,3-dinitro-1,3-butadiene 1 with benzyl Grignard reagents

The above-cited transformations of the bis(diethylamino) derivative **1** into compounds **2** via an overall substitution of the dialkylamino groups by the residues of Grignard reagents show that the two *tert*-nitroenamine moieties of **1** in spite of being in a conjugated position behave independently as monofunctional systems. Accordingly, the



1 (75%)

2 (60-95%)

2a: R = alkyl; **2b**: R = aryl; **2c**: R = vinyl, 2-arylvinyl

Scheme 1. *Reagents and conditions*: (a) Excess Et_2NH (4 mol equiv.), EtOH, 0–25°C; (b) RMgX (2.2 mol equiv.), THF, 0°C; (c) Ice/excess HCl quenching.

[☆] See Ref. 1.

Keywords: nitroenamines; nitrohexatrienes; electrocyclization; diarylnitrobenzenes.

[*] Corresponding author. Tel.: +39-010-3536122; fax: +39-010-3624337; e-mail: tavani@chimica.unige.it

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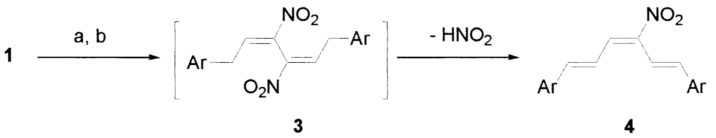


a: Ar = C_6H_5
b: Ar = 4-MeC_6H_4
c: Ar = 3-$MeOC_6H_4$
d: Ar = 4-$MeOC_6H_4$
e: Ar = 2-thienyl
f: Ar = 3-thienyl

Scheme 2. *Reagents and conditions*: (a) Excess $ArCH_2MgCl$ (4 mol equiv.), THF, 0°C; (b) H_3O^+ quenching.

reported reaction[7] of 2-dimethylamino-1-nitro-1-phenylethylene with benzylmagnesium chloride to give 1-nitro-1,3-diphenylpropylene suggested the possibility that a consistent transformation (Scheme 2) of **1** into 1,6-diaryl-3,4-dinitro-2,4-hexadienes **3** could occur by reaction with arylmethylmagnesium chlorides.

In a typical experiment 1 mmol of the bis(diethylamino)-dinitrobutadiene **1** in THF was reacted, at 0°C and under argon, with an excess (4 mmol) of freshly prepared arylmethylmagnesium chloride (ca. 1 M in THF). After about 15 min, TLC of aliquots of the reaction mixture quenched into ice/HCl and extracted with ether revealed (besides 1,2-diarylethane by-products resulting from the preparation of the Grignard)[8–10] complete disappearance of the substrate **1** and the presence of a main colourless product, presumably the expected bisbenzyl derivative **3**. Quenching of the reaction mixture into ice and excess HCl (quenching A, analogous to that employed for the reactions of **1** with other kinds of Grignard reagents)[2–4] and usual work-up did not allow isolation of even traces of the expected derivatives **3**. Actually, in a short time the reaction extracts turned red, a colour change observed even on the colourless TLC spot and on silica gel column during chromatography, and the only isolable products were (Scheme 2) the red 1,6-diaryl-3-nitro-1,3,5-hexatrienes **4a–d** (Table 1, quenching A) identified through their microanalytical and ^1H and ^{13}C NMR spectroscopic data.

Table 1. Yields of 1,6-diaryl-3-nitro-1,3,5-hexatrienes **4** from the reactions of 1,4-bis(diethylamino)-2,3-dinitro-1,3-butadiene **1** with arylmethylmagnesium chlorides

Product	Yields (%)[a]	
	Quenching A[b,c]	Quenching B[d,e]
4a	46	76
4b	45	72
4c	50	78
4d	43	73
4e	–	41
4f	–	45

[**1**]≈0.03 M, [$ArCH_2MgCl$]≈0.12 M, THF, 0°C.

[a] Yields of products, isolated by chromatography, essentially pure by ^1H NMR spectroscopy.

[b] Quenching with ice and excess HCl.

[c] The yields reported refer to the best values obtained; with quenching A the yields were hardly reproducible in duplicate experiments and values as low as 20% were sometimes obtained.

[d] Quenching with dichloromethane/ice and 0.1 M HCl (1 mol per mol of Grignard employed).

[e] Average values of at least two independent experiments.

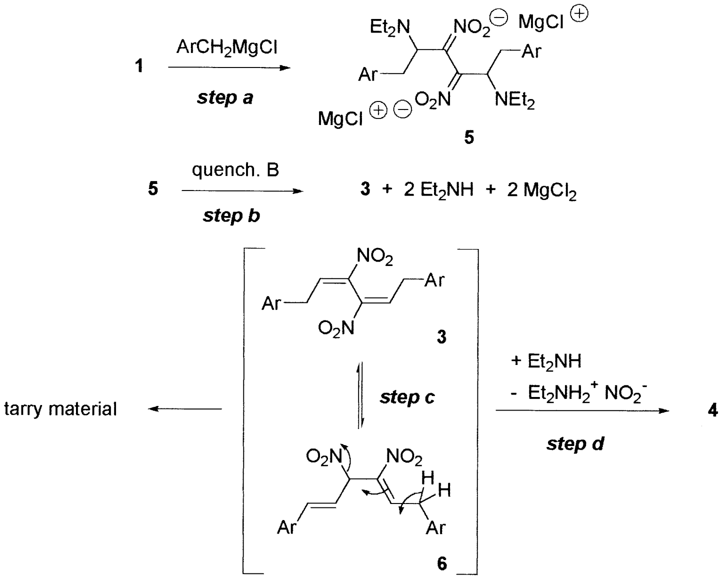
Common features of the studied reactions were that: (a) in spite of several attempts, changing both the reaction and the work-up conditions, we were never able to isolate the expected 1,6-diaryl-3,4-dinitro-2,4-hexadienes **3**; (b) among numerous duplicate experiments carried out under similar conditions (quenching A), the yields of **4a–d** were hardly reproducible in spite of careful workup.[11] In this regard it should be stressed that the yields reported in Table 1 for quenching A refer to the best ones obtained and that values as low as 20% were sometimes obtained.

When the mixtures of the reactions of **1** with benzyl Grignard reagents were poured into dichloromethane/ice containing 0.1 M HCl in a stoichiometric amount with respect to the Grignard employed (quenching B) the formation of compounds **4a–d** (as judged by the appearance of a deep red colour) was at a glance faster. Under these conditions the yields of **4a–d**, while made more reproducible in duplicate experiments, were substantially improved (Table 1, quenching B) and the method was therefore extended to the synthesis of the thienyl derivatives **4e** and **4f** for which preliminary experiments through quenching A gave very discouraging results.

The above results can be well explained in light of the most likely mechanism for the overall transformation of **1** into **4** (Scheme 3).

Thus, in agreement with previous findings[2–4] and with the outcomes on monofunctional *tert*-nitroenamine systems,[7] the first step of the reaction (Scheme 3, step a) should involve a double 1,4-addition of the Grignard reagent to the nitrovinyl systems of **1**. By acidic quenching the intermediate dinitronate **5** should eliminate (step b) two molecules of diethylamine to furnish the 1,6-diaryl-3,4-dinitro-2,4-hexadiene **3**. A nitrovinyl to nitroallyl tautomerisation[12,13] of **3** into **6** (step c) followed by nitrous acid elimination (step d) would eventually give the isolated nitrohexatriene **4**. In agreement with the expected base effect in the latter steps, the obtained results indicate that the presence of free diethylamine during quenching plays a fundamental role for an efficient formation of **4**. Consistently, under quenching A conditions, the excess HCl subtracting free amine, the formation of **4** becomes slow and occurs with hardly reproducible yields because of competitive formation of tarry material.

As regards stereochemistry of the isolated 1,6-diaryl-3-nitro-1,3,5-hexatrienes **4** a (1*E*,3*E*,5*E*)-configuration can be confidently assigned by analogy on the grounds of the following data: (a) when practically detectable in the ^1H



Scheme 3. Possible mechanism accounting for the transformation of **1** into **4**.

NMR spectra, the values (ca. 15–16 Hz) of $J_{H-C(1), H-C(2)}$ and of $J_{H-C(5), H-C(6)}$ indicate a *trans*-relation between the relevant protons; (b) the high deshielding for H–C(4) suggests,[2–4,6] that this proton is *cis* to the nitro group; (c) an X-ray crystal structure analysis of compound **4b** (Fig. 1) confirmed the (1*E*,3*E*,5*E*)-configuration attributable on the grounds of the ^{1}H NMR outcomes.

2.2. Synthesis of 1,2-diaryl-4-nitrobenzenes 8a–f via oxidative electrocyclization of 4a–f

The chemical behaviour and the application scope of 1,3,5-hexatrienes are obviously connected with the presence of a conjugated 6π-electron system. Such a characteristic, besides being interesting, e.g. for spectroscopic studies of 1,3,5-hexatriene derivatives as LCS models (linear π-conjugated systems)[15–18] and for their use as fluorescence probes,[19] is important in synthesis because of the possibility for 1,3,5-hexatrienes of undergoing thermally- or photochemically-induced 6π-electrocyclization to the corresponding 1,3-cyclohexadienes.[20,21] Such electrocyclic interconversion between the hexatriene and the cyclohexadiene system has been very recently exploited[22] for the thermal synthesis of benzene derivatives from (*E*,*E*,*E*)-1-chloro-1,3,5-alkatrienes, thanks to the spontaneous HCl elimination following ring closure. In general, besides other factors (e.g. low periselectivity), the synthetic utility of such electrocyclisations is sometimes limited by the fact that the presence of *cis*-configuration of the central, C(3)–C(4), double bond is a fundamental requisite for an efficient cyclisation.

In light of the favourable *cis*-configuration of the C(3)–C(4) double bond the possibility for the hexatrienes **4a–f** to undergo (Scheme 4) thermally-induced 6π-electrocyclization to the corresponding 5,6-diaryl-2-nitro-1,3-cyclohexadienes **7a–f** was first checked by ^{1}H NMR spectroscopy of samples of **4a–f** heated in $CDCl_3$ at 60°C in the NMR tube.

In all cases, the occurence of electrocyclization of **4a–f** was

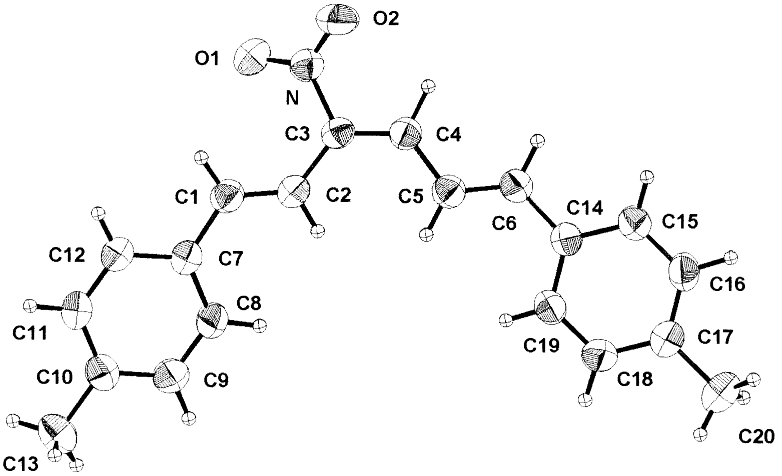
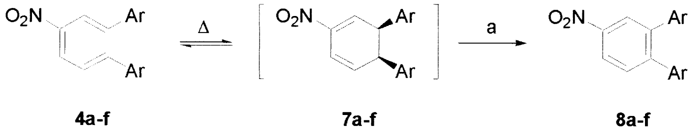


Figure 1. ORTEP drawing[14] of **4b**, with numbering of atoms. Displacement ellipsoids are drawn at 50% probability level; hydrogen atoms, treated as isotropic, are on an arbitrary scale.



Scheme 4. *Reagents and conditions*: (a) DDQ or I_2/cyclohexene oxide, toluene, 80°C, overnight (routine).

evidenced by the progressive formation of the corresponding **7a–f** characterised, in particular, by absorptions at δ 3.9–4.3, 4.2–4.5 and 6.1–6.2 ppm for H–C(5), H–C(6) and H–C(4), respectively [H–C(1) and H–C(3) being sometimes masked by the aromatic protons]. The $J_{\text{H–C(5), H–C(6)}}$ average value of ca. 9.8 Hz suggests[23] a *cis*-relation between the two protons that, on the other hand, is in agreement with a disrotatory cyclization of **4** to **7** predictable on the grounds of the Woodward–Hoffmann rule.[24–26]

Whereas no attempt was made of isolating the cyclohexadiene intermediates **7a–f**, the nitrohexatrienes **4a–f** were subjected to oxidative cyclization in toluene at 80°C either with DDQ (method A) or with iodine (method B) as oxidants, the latter in the presence of cyclohexene oxide as HI-scavenger.[27,28] As reported in Table 2 such reactions, routinely carried out overnight, gave good yields of 1,2-diaryl-4-nitrobenzenes **8a–f** (Scheme 4), method B appearing preferable to method A generally because of an easier, smoother workup. With reference to the use of an epoxide as HI scavenger in method B, it should be mentioned that preliminary experiments carried out on **4a** with iodine alone showed the formation of 68% yield of **8a** and 20% yield of the corresponding 3,4-diphenylaniline,[29] most likely resulting from reduction of **8a** by HI in the used conditions.

Table 2. Yields of 1,2-diaryl-4-nitrobenzenes **8** from oxidative electrocyclization of the corresponding 1,6-diaryl-3-nitro-1,3,5-hexatrienes **4**

Product	Yields (%)[a]	
	Method A[b]	Method B[c]
8a	75	92
8b	88	96
8c	84	80
8d	78	85
8e	–	95
8f	83	98

[a] Isolated yields, average values of at least two independent experiments performed routinely overnight.

[b] Method A: DDQ (1.1 mol. equiv.) in toluene at 80°C.

[c] Method B: Iodine (5 mol. equiv.) and cyclohexene oxide (2 mol. equiv.) in toluene at 80°C.

3. Conclusion

In conclusion, following the ring-opening of 3,4-dinitrothiophene with diethylamine, simple procedures characterised by generally good yields allow the synthesis of hitherto unknown interesting compounds such as nitrohexatrienes **4a–f** and 1,2-diaryl-4-nitrobenzenes **8a–f** which would be very difficult (perhaps impossible in some cases) to prepare by conventional methods. For instance, it is worth noting that 1,2-diphenyl-4-nitrobenzene **8a** was already isolated[30] through troublesome separation procedures from complex mixtures obtained from nitration of *o*-terphenyl. It is plain that, provided the corresponding 1,2-diarylbenzenes were available, the same nitration procedure would not be applicable to the synthesis of **8b–f**, owing to the higher reactivity of the *p*-tolyl, of the *m*- and *p*-anisyl and of the 2- and 3-thienyl rings to electrophylic substitutions.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer with TMS as internal reference; chemical shifts are expressed as δ ppm. IR spectra were registered on a Perkin–Elmer 881 spectrophotometer. Melting points were determined on a Büchi 535 apparatus and are uncorrected. Silica gel 230–400 mesh was used for column chromatography. All solvents were distilled before use; petroleum ether and light petroleum refer, respectively, to the fraction with bp 40–60 and 80–100°C. Tetrahydrofuran (THF) was purified by standard methods and distilled over potassium benzophenone ketyl before use. Commercial benzyl, 4-methyl-, 3- and 4-methoxybenzyl chlorides were distilled before use; 2-[31] and 3-chloromethylthiophene[32] were prepared following literature procedures. 1,4-Bis(diethylamino)-2,3-dinitro-1,3-butadiene **1** was synthesised from 3,4-dinitrothiophene as reported.[3] All other commercially available reagents were used as received.

4.2. Arylmethylmagnesium chlorides and 1,2-diarylethanes

Solutions of arylmethylmagnesium chlorides (ca. 1 M in THF) were generally prepared by standard methods from freshly distilled benzyl chlorides (10 mmol) and magnesium turnings (0.73 g). For the preparation of ca. 0.6 M solutions of 2- and 3-thienylmethylmagnesium chlorides, better results were obtained by the use of a five-fold excess of Mg turnings with respect to the thenyl chloride and a mixture (ca. 5:1, v/v) of THF and xylene as solvent. Before use, the reagents were titrated[33] and aliquots of the solutions poured into ice/HCl in order to obtain samples of the 1,2-diarylethane byproducts, which were identified by comparison (mp and/or ^{1}H NMR) with literature data.[31,34–39]

4.3. Reactions of 1,4-bis(diethylamino)-2,3-dinitro-1,3-butadiene 1 with benzyl Grignard reagents

In a flame-dried two-neck flask, equipped with an argon inlet, a rubber septum and a magnetic stirring bar, 0.29 g (1 mmol) of 1,4-bis(diethylamino)-2,3-dinitro-1,3-butadiene were suspended in 30 mL of THF and cooled to ca. 0°C with an external ice bath; the Grignard reagent in THF

(4 mmol) was slowly added by syringe under magnetic stirring. The reaction mixture was kept at the same temperature for 15 min (the end of reaction being judged by TLC analysis), then poured with stirring (quenching B) into a dichloromethane/ice/HCl (4 mmol) mixture. After separation of the two layers, the aqueous phase was extracted with dichloromethane and the organic phase washed with water, then dried over Na_2SO_4. Concentration under vacuum of the extracts[11] gave a crude which was purified by column chromatography over silica gel (petroleum ether/dichloromethane gradients as eluent). Yields of products **4** are collected in Table 1 (quenching B).

Pouring of the reaction mixture into ice and excess HCl (quenching A, Table 1) resulted in lower and hardly reproducible yields of **4**.

4.3.1. (*E*,*E*,*E*)-1,6-Diphenyl-3-nitro-1,3,5-hexatriene (4a). Red solid, mp 122.6–122.8°C (EtOH). ν_{max} (Nujol) 1594, 1500, 1326, 1316, 1161 cm^{-1}. ^1H NMR: δ 7.00 and 7.09 (1H each, AB, J=16.6 Hz), 7.16 and 7.23 (2H, AB of ABX, J_{AB}=16.1 Hz, J_{AX}=6.7 Hz, J_{BX}=4.7 Hz), 7.39 and 7.53 (10H in all, two m partially overlapped), 7.80 (1H, X of ABX, $J_{AX}+J_{BX}$=11.4 Hz). ^{13}C NMR: δ 116.42, 121.94, 127.11, 127.67, 128.90, 129.01, 129.18, 130.00, 133.75, 135.69, 135.94, 137.62, 144.77, 147.62. Anal. Calcd for $C_{18}H_{15}NO_2$: C, 78.0; H, 5.5; N, 5.1%. Found: C, 78.2; H, 5.5; N, 5.2%.

4.3.2. (*E*,*E*,*E*)-1,6-Bis(4-methylphenyl)-3-nitro-1,3,5-hexatriene (4b). Red solid, mp 115.6–116.8°C (EtOH). ν_{max} (Nujol) 1585, 1500, 1332, 1314, 1166 cm^{-1}. ^1H NMR: δ 2.37 and 2.40 (6H in all, two s partially overlapped), 6.94 and 7.05 (1H each, AB, J=16.4 Hz), 7.19 (6H, m), 7.43 (4H, m), 7.79 (1H, X of ABX, $J_{AX}+J_{BX}$=10.8 Hz). ^{13}C NMR: δ 21.35, 21.47, 115.63, 121.23, 127.09, 127.68, 129.64, 129.78, 133.24, 133.46, 133.64, 137.42, 139.34, 140.45, 144.60, 147.54. Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.7; H, 6.3; N, 4.6%. Found: C, 79.0; H, 6.4; N, 4.5%.

4.3.3. (*E*,*E*,*E*)-1,6-Bis(3-methoxyphenyl)-3-nitro-1,3,5-hexatriene (4c). Red solid, mp 79.0–79.8°C (petroleum ether). ν_{max} (Nujol) 1600, 1573, 1505, 1487, 1315, 1264, 1184, 1156, 1039 cm^{-1}. ^1H NMR: δ 3.83 (3H, s), 3.87 (3H, s), 6.92, 7.03 and 7.14 (10H in all, three m partially overlapped), 7.28 and 7.31 (2H, AB of ABX, J_{AB}=16.2 Hz, J_{AX}=4.7 Hz, J_{BX}=5.0 Hz), 7.79 (1H, X of ABX, $J_{AX}+J_{BX}$=9.7 Hz). ^{13}C NMR: δ 55.32, 55.39, 112.34, 113.21, 114.90, 115.48, 116.66, 119.78, 120.19, 122.24, 129.89, 130.02, 133.68, 137.10, 137.37, 137.57, 144.71, 147.65, 160.02. Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.2; H, 5.7; N, 4.2%. Found: C, 71.3; H, 5.9; N, 4.2%.

4.3.4. (*E*,*E*,*E*)-1,6-Bis(4-methoxyphenyl)-3-nitro-1,3,5-hexatriene (4d). Red solid, mp 134.5–135.7°C (dichloromethane/petroleum ether). ν_{max} (Nujol) 1602, 1587, 1508, 1324, 1301, 1282, 1251, 1174, 1030 cm^{-1}. ^1H NMR: δ 3.84 and 3.86 (6H in all, two s partially overlapped), 6.92 (6H, m), 7.04 and 7.14 (2H, AB of ABX, J_{AB}=15.8 Hz, J_{AX}=10.6 Hz, J_{BX}=1.0 Hz), 7.48 (4H, two halves of AA′BB′ partially overlapped, J=8.8 Hz), 7.77 (1H, X of ABX, $J_{AX}+J_{BX}$=11.6 Hz). ^{13}C NMR: δ 55.46, 114.41, 114.52, 114.58, 120.12, 128.51, 128.83, 129.05, 129.34, 133.75, 136.72, 144.23, 147.04, 160.52, 161.26. Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.2; H, 5.7; N, 4.2%. Found: C, 71.4; H, 5.9; N, 4.4%.

4.3.5. (*E*,*E*,*E*)-1,6-Bis(2-thienyl)-3-nitro-1,3,5-hexatriene (4e). Red solid, mp 91.2–92.5°C (dichloromethane/petroleum ether). ν_{max} (Nujol) 1616, 1587, 1500, 1310, 1218, 1162, 1078, 1023 cm^{-1}. ^1H NMR: δ 6.87 and 6.93 [2H in all, half AB (J=16.2 Hz) partly overlapped with a dd (J=11.8 and 15.0 Hz)], 7.06 (2H, m), 7.20 (4H, m), 7.34 (1H. m), 7.39 (1H, d, J=5.2 Hz), 7.69 (1H, d, J=11.8 Hz). ^{13}C NMR: δ 115.18, 121.17, 126.67, 127.99, 128.43, 129.94, 130.03, 133.20, 136.95, 141.41, 141.53, 146.47. Anal. Calcd for $C_{14}H_{11}NO_2S_2$: C, 58.1; H, 3.8; N, 4.8%. Found: C, 58.3; H, 3.9; N, 4.9%.

4.3.6. (*E*,*E*,*E*)-1,6-Bis(3-thienyl)-3-nitro-1,3,5-hexatriene (4f). Red solid, mp 93.5–94.8°C (dichloromethane/petroleum ether). ν_{max} (Nujol) 1597, 1494, 1310, 1294, 1239, 1186, 1149, 1027 cm^{-1}. ^1H NMR: δ 6.95 and 6.96 [3H in all, AB system (J=16.2 Hz) partly overlapped with a dd (J=11.4 and 15.4 Hz)], 7.33 (5H, m), 7.46 (1H, dd, J=1.4 and 2.6 Hz), 7.73 (1H, d, J=11.4 Hz). ^{13}C NMR: δ 116.24, 121.97, 124.83, 125.01, 125.08, 126.85, 127.09, 127.14, 131.33, 133.75, 138.19, 139.01, 139.06, 147.14. Anal. Calcd for $C_{14}H_{11}NO_2S_2$: C, 58.1; H, 3.8; N, 4.8%. Found: C, 58.2; H, 3.7; N, 4.9%.

4.4. Crystal structure determination of compound 4b

Crystallographic data of **4b** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163772. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Rd., Cambridge CB2 1EZ, UK (fax: +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

4.5. ^1H NMR evidence for the formation of *cis*-5,6-diaryl-2-nitro-1,3-cyclohexadienes 7a–f from the corresponding hexatrienes 4a–f

Solutions in $CDCl_3$ of the hexatrienes **4a**–**f** were heated at 60°C for 3–9 h in the NMR tube; ^1H NMR spectra were registered at different times, after cooling at room temperature. The data given below refer to absorptions that can be confidently attributed to compounds **7a**–**f**. Lacking data are due to overlapping of signals with those of traces either of the starting hexatriene or of the corresponding 1,2-diaryl-4-nitrobenzene **8**.

4.5.1. 5,6-Diphenyl-2-nitro-1,3-cyclohexadiene 7a. ^1H NMR: δ 3.92 (1H, ddd, $J_{3,5}$=1.8 Hz, $J_{4,5}$=4.4 Hz, $J_{5,6}$=10.2 Hz, *H-5*), 4.19 (1H, dd, $J_{1,6}$=4.4 Hz, $J_{5,6}$=10.2 Hz, *H-6*), 6.14 (1H, dd, $J_{4,5}$=4.4 Hz, $J_{3,4}$=10.0 Hz, *H-4*).

4.5.2. 5,6-Bis(4-methylphenyl)-2-nitro-1,3-cyclohexadiene 7b. ^1H NMR: δ 2.25 and 2.26 (6H in all, two partly overlapped s, 2×*Me*), 3.93 (1H, ddd, $J_{3,5}$=2.0 Hz, $J_{4,5}$=4.5 Hz, $J_{5,6}$=9.9 Hz, *H-5*), 4.19 (1H, dd, $J_{1,6}$=4.4 Hz, $J_{5,6}$=9.9 Hz, *H-6*), 6.19 (1H, dd, $J_{4,5}$=4.5 Hz, $J_{3,4}$=10.0 Hz, *H-4*), 6.65 (4H, two partly overlapped AA′ of AA′BB′, 4H_{arom}), 6.90 (5H, m and two partly overlapped BB′ of AA′BB′,

$4H_{\text{arom}}$ and *H-3*), 7.24 [≈1H, dd ($J_{1,3}$=1.8 Hz, $J_{1,6}$=4.4 Hz) partly masked by the $CHCl_3$ signal, *H-1*].

4.5.3. 5,6-Bis(3-methoxyphenyl)-2-nitro-1,3-cyclohexadiene 7c. ^{1}H NMR: δ 3.58 and 3.60 (6H in all, two partly overlapped s, 2×*MeO*), 3.97 (1H, ddd, $J_{3,5}$=2.0 Hz, $J_{4,5}$= 4.5 Hz, $J_{5,6}$=10.1 Hz, *H-5*), 4.23 (1H, dd, $J_{1,6}$= 4.5 Hz, $J_{5,6}$=10.1 Hz, *H-6*), 6.22 [3H in all, dd ($J_{4,5}$= 4.5 Hz, $J_{3,4}$=10.2 Hz) partly overlapped to a m, $2H_{\text{arom}}$ and *H-4*), 6.44 (2H, m, $2H_{\text{arom}}$), 6.70 (2H, m, $2H_{\text{arom}}$), 6.94 (1H, dt, $J_{1,3}$=$J_{3,5}$=2.0 Hz, $J_{3,4}$=10.2 Hz, *H-3*), 7.05 [2H in all, two partly overlapped t (*J*=7.9 Hz), $2H_{\text{arom}}$], 7.24 [≈1H, dd ($J_{1,3}$=2.0 Hz and $J_{1,6}$=4.5 Hz)) partly masked by the $CHCl_3$ signal, *H-1*].

4.5.4. 5,6-Bis(4-methoxyphenyl)-2-nitro-1,3-cyclohexadiene 7d. ^{1}H NMR: δ 3.73 and 3.74 (6H in all, two partly overlapped s, 2×*MeO*), 3.90 (1H, ddd, $J_{3,5}$=2.1 Hz, $J_{4,5}$= 4.5 Hz, $J_{5,6}$=10.0 Hz, *H-5*), 4.16 (1H, dd, $J_{1,6}$=4.5 Hz, $J_{5,6}$=10.0 Hz, *H-6*), 6.16 (1H, dd, $J_{4,5}$=4.5 Hz, $J_{3,4}$= 10.3 Hz, *H-4*), 6.64 and 6.67 (8H in all, two partly overlapped br s, $8H_{\text{arom}}$), 7.24 (1H, dd, $J_{1,3}$=1.5 Hz, $J_{1,6}$=4.5 Hz, *H-1*].

4.5.5. 5,6-Bis(2-thienyl)-2-nitro-1,3-cyclohexadiene 7e. ^{1}H NMR: δ 4.31 (1H, ddd, $J_{3,5}$=2.1 Hz, $J_{4,5}$=4.4 Hz, $J_{5,6}$=9.1 Hz, *H-5*), 4.52 (1H, dd, $J_{1,6}$=4.6 Hz, $J_{5,6}$=9.1 Hz, *H-6*), 6.27 (1H, dd, $J_{4,5}$=4.4 Hz, $J_{3,4}$=10.2 Hz, *H-4*), 6.59 (1H, m, $1H_{\text{arom}}$), 6.66 (1H, m, $1H_{\text{arom}}$).

4.5.6. 5,6-Bis(3-thienyl)-2-nitro-1,3-cyclohexadiene 7f. ^{1}H NMR: δ 4.09 (1H, ddd, $J_{3,5}$=2.0 Hz, $J_{4,5}$=4.5 Hz, $J_{5,6}$=9.4 Hz, *H-5*), 4.33 (1H, dd, $J_{1,6}$=4.6 Hz, $J_{5,6}$=9.4 Hz, *H-6*), 6.21 (1H, dd, $J_{4,5}$=4.5 Hz, $J_{3,4}$=10.0 Hz, *H-4*), 6.48 (1H, dd, *J*=1.4 and 4.8 Hz, $1H_{\text{arom}}$), 6.59 (1H, dd, *J*=1.4 and 4.8 Hz, $1H_{\text{arom}}$), 6.72 (1H, m, $1H_{\text{arom}}$), 6.77 (1H, m, $1H_{\text{arom}}$), 6.88 (1H, dt, $J_{1,3}$=$J_{3,5}$=2.0 Hz, $J_{3,4}$=10.0 Hz, *H-3*), 7.13 [2H in all, two dd partly overlapped (*J*=3.2 and 5.0 Hz) (*J*=2.9 and 5.1 Hz), $2H_{\text{arom}}$], 7.24 [≈1H, dd ($J_{1,3}$=2.0 Hz, $J_{1,6}$=4.6 Hz) partly masked by the $CHCl_3$ signal, *H-1*].

4.6. Oxidative electrocyclizations of hexatrienes 4a–f

Method A. In a flask, equipped with a magnetic stirring-bar and a reflux condenser, a solution of the hexatriene **4** (0.16 mmol) and DDQ (0.18 mmol) in dry toluene (4 mL) was heated at 80°C overnight. The cold reaction mixture was diluted with diethyl ether, filtered, washed with an aqueous $NaHCO_3$ saturated solution, with water, and dried over Na_2SO_4. Filtration and removal of the solvent under reduced pressure furnished a residue which was purified by column chromatography. Relevant yields of the products **8** are collected in Table 2.

Method B. In a flask, equipped with a magnetic stirring-bar and a reflux condenser with a silica-gel trap, 0.4 mmol of **4** were dissolved in 500 mL of dry toluene. Cyclohexene oxide (0.8 mmol) and I_2 (2 mmol) were added and the reaction mixture heated at 80°C overnight. The cold reaction solution was washed with a 5% NaOH aqueous solution, with water and dried over Na_2SO_4. Filtration and removal of the solvent under reduced pressure furnished a residue which was usually purified by column chromatography. Relevant yields of the products **8** are collected in Table 2.

4.6.1. 1,2-Diphenyl-4-nitrobenzene 8a. Yellow solid, mp 117.5–118.0°C (petroleum ether) (lit.[30] mp 118.3–118.5°C).

4.6.2. 1,2-Bis(4-methylphenyl)-4-nitrobenzene 8b. Yellow solid, mp 130.0–131.0°C (light petroleum). ν_{max} (Nujol) 1608, 1581, 1510, 1349, 1186, 1102 cm^{-1}. ^{1}H NMR: δ 2.33 (6H, s), 7.05 (4H, two AA′BB′, *J*=8.7 Hz), 7.54 (1H, d, *J*=8.4 Hz), 8.20 (1H, dd, *J*=2.4 and 8.4 Hz), 8.26 (1H, d, *J*=2.4 Hz). ^{13}C NMR: δ 21.18, 29.70, 121.98, 125.56, 128.98, 129.02, 129.41, 129.47, 131.49, 136.54, 136.61, 137.29, 137.59, 141.78, 146.98. Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.2; H, 5.7; N, 4.6%. Found C, 79.4; H, 5.9; N, 4.7%.

4.6.3. 1,2-Bis(3-methoxyphenyl)-4-nitrobenzene 8c. Yellow solid, mp 96.3–97.5°C (petroleum ether). ν_{max} (Nujol) 1601, 1587, 1513, 1342, 1324, 1309, 1292, 1269, 1224, 1188, 1028 cm^{-1}. ^{1}H NMR: δ 3.64 and 3.65 (6H in all, two s partially overlapped), 6.66 (2H, m), 6.79 (4H, m), 7.19 (2H, app. t, *J*=7.9 Hz), 7.59 (1H, d, *J*=8.4 Hz), 8.25 (1H, dd, *J*= 2.6 and 8.4 Hz), 8.31 (1H, d, *J*=2.6 Hz). ^{13}C NMR: δ 55.20, 113.61, 113.78, 114.92, 114.96, 121.91, 122.02, 122.30, 125.37, 129.34, 129.39, 131.38, 140.64, 140.71, 141.80, 146.86, 147.15, 159.33, 159.40. Anal. Calcd for $C_{20}H_{17}NO_4$: C, 71.6; H, 5.1; N, 4.2%. Found: C, 71.8; H, 5.1; N, 4.2%.

4.6.4. 1,2-Bis(4-methoxyphenyl)-4-nitrobenzene 8d. Yellow solid, mp 118.0–119.5°C (dichloromethane/petroleum ether). ν_{max} (Nujol) 1608, 1566, 1507, 1348, 1296, 1256, 1178, 1046, 1024 cm^{-1}. ^{1}H NMR: δ 3.80 (6H, s), 6.80 [4H in all, two AA′ of AA′BB′ (*J*=8.8 and 8.9 Hz) partially overlapped], 7.08 (4H, two BB′ of AA′BB′ overlapped), 7.52 (1H, d, *J*=8.4 Hz), 8.19 (1H, dd, *J*=2.4 and 8.4 Hz), 8.25 (1H, d, *J*=2.4 Hz). ^{13}C NMR: δ 55.23, 113.81, 121.88, 125.48, 130.78, 131.33, 131.86, 141.32, 146.60, 146.83, 159.01, 159.23. Anal. Calcd for $C_{20}H_{17}NO_4$: C, 71.6; H, 5.1; N, 4.2%. Found C, 71.3; H, 5.0; N, 4.3%.

4.6.5. 1,2-Bis(2-thienyl)-4-nitrobenzene 8e. Yellow solid, mp 61.0–61.8°C (petroleum ether). ν_{max} (Nujol) 1596, 1570, 1510, 1349, 1271, 1249, 1105, 1087, 1051 cm^{-1}. ^{1}H NMR: δ 7.02 (4H, m), 7.37 (2H, m), 7.68 (1H, d, *J*=8.5 Hz), 8.20 (1H, dd, *J*=2.5 and 8.5 Hz), 8.35 (1H, d, *J*=2.5 Hz). ^{13}C NMR: δ 122.67, 126.16, 127.31, 127.38, 127.42, 127.96, 128.27, 128.49, 131.49, 134.88, 140.10, 140.21, 140.41, 146.83. Anal. Calcd for $C_{14}H_9NO_2S_2$: C, 58.5; H, 3.2; N, 4.9%. Found C, 58.8; H, 3.4; N, 4.9%.

4.6.6. 1,2-Bis(3-thienyl)-4-nitrobenzene 8f. Yellow solid, mp 117.3–118.5°C (light petroleum). ν_{max} (Nujol) 1601, 1573, 1510, 1344, 1269, 1105, 1088 cm^{-1}. ^{1}H NMR: δ 6.81 (2H, m), 7.19 (2H, m), 7.25 (2H, m), 7.60 (1H, d, *J*=8.4 Hz), 8.19 (1H, dd, *J*=2.6 and 8.4 Hz), 8.31 (1H, d, *J*=2.6 Hz). ^{13}C NMR: δ 122.22, 124.19, 124.63, 125.18, 125.67, 125.70, 128.26, 128.30, 130.95, 136.63, 139.86, 139.93, 141.72, 146.99. Anal. Calcd for $C_{14}H_9NO_2S_2$: C, 58.5; H, 3.2; N, 4.9%. Found C, 58.8; H, 3.3; N, 4.8%.

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11. The possibility for compounds **4** to easily undergo 6π electrocyclization to the corresponding 5,6-diaryl-2-nitro-1,3-cyclohexadienes **7** (see text) enforces the use of careful workup and purification procedures. Heating of reaction extracts and of chromatographic fractions should be avoided as well as during crystallization of compounds **4**. The use of crude chromatographic samples of **4** for successive reactions is sometimes preferable.
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