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3-Nitrocoumarins as Dienophiles in the Diels−Alder Reaction in Water. An Approach to the Synthesis of Nitrotetrahydrobenzo[c]chromenones and Dihydrodibenzo[b,d]furans

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The [4 + 2] cycloadditions of 3-nitrocoumarin (**1a**), 6-chloro-3-nitrocoumarin (**1b**), and 6-, 7-, and 8-hydroxy-3-nitrocoumarins (**1c**, **5**, and **6**) with (*E*)-piperylene (**7**), isoprene (**8**), 2,3-dimethyl-1,3-butadiene (**9**), 2-methoxy-1,3-butadiene (**10**), 2,3-dimethoxy-1,3-butadiene (**11**), and cyclopentadiene (**12**) were investigated in aqueous medium, in organic solvent and under solventless conditions. The reactions performed in water occurred in heterogeneous phase but were faster than those executed in toluene or dichloroethane (DCE). **1a**−**c**, **5**, and **6** behaved as 2π components in the Diels−Alder cycloadditions with **7**−**10** and **12**, and exo adducts were preferentially or exclusively produced. Surprisingly **1a**, behaved as a 4π component in the cycloaddition in water with **11** and 4-substituted 3-nitrochromanones **20** and **21** were isolated. The cycloadditions of hydroxy-3-nitrocoumarins **1c**, **5**, and **6** with 1,3-diene **9** did not work in water or in organic solvent, but did work under solventless conditions. Nitrotetrahydrobenzo[c]chromenones **13**−**16**, **24**, and **25**, originating from the *normal* electron-demand Diels−Alder reactions, were converted into dihydrodibenzo[b,d]furans **27**−**31** in water, *via* one-pot Nef-cyclodehydration reactions.

Introduction

The consciousness of the importance of environmental issues and energy-related problems, have driven basic chemical research to devise new processes and new reaction methodologies. Reactions carried out in water, in solventless conditions, under high pressure, in super-critical fluids, in ionic liquids, in microemulsion, and by using ultrasound and microwaves have furthered basic chemical knowledge and contributed to the development of new processes that reduce pollution at the source.[1]

Water as a reaction medium has particularly captured the interest of organic chemists,[1c,d,f,g,2] and reactions previously thought impossible in water are nowadays a reality. Many Lewis acids work well in aqueous media,[1f,2c−i] and recently we found that even AlCl$_3$, SnCl$_4$, and TiCl$_4$, recommended for use under anhydrous conditions are excellent catalysts in water.[3] One of the greatest advantages of aqueous media,[2f] with respect to organic solvents, is the possibility to control and change the pH. This affects the acid/base equilibria and the nature and concentration of the active species, with dramatic effects on reaction rates and product selectivities.[4] It also allows one-pot processes to be carried out by consecutive procedures.[5]

Our interest in organic reactions carried out exclusively in water[2f,h,i,3−6] led us to investigate the [4 + 2] cycloadditions of α,β-unsaturated nitrocompounds[6c] (α-nitroalkenes) and the use of a special class of these compounds, the 3-nitrocoumarins, as building blocks for organic reactions performed in aqueous media.[6e]

To our knowledge, 3-nitrocoumarins have rarely been used as 4π components or as building blocks[6e] and have

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never been used as 2π components, although they are a promising starting material for the synthesis of functionalized α-amino acids. Some examples involving 3-substituted coumarins such as 3-alkoxycarbonyl,[7a−d] 3-carbonyl,[7d] 3-vinyl,[7e] and 3-cyano[7b,f] derivatives have been reported.

α-Nitroalkenes are attractive building blocks because they can be used as 4π or 2π components in [4 + 2] cycloadditions[6e,8,9] and as Michael acceptors[10] and the nitro functionality can be easily converted to an amino or a carbonyl group.[11] While the use of α-nitroalkenes as 4π components has been widely investigated,[8] their behavior as 2π components has only been sporadically studied.[9]

Recent papers from this laboratory[6c,e] have described the use of α-nitroalkenes as 4π components in [4 + 2] cycloadditions in water. The reactions occurred in a fast and highly endo-selective way in heterogeneous phase under mild conditions without the use of catalysts. (*E*)-2-Aryl-1-cyano-1-nitroethenes gave highly asymmetric cycloadditions,[6c] and 3-nitrocoumarins allowed chromene derivatives to be prepared by a one-pot procedure.[6e]

On the basis of (a) the possibility that a δ-nitro alcohol could be converted into a dihydrofuran derivative via one-pot Nef-cyclodehydration reactions carried out in water

and (b) the results of our recent work[6e] where [4 + 2] cycloadducts coming from the reaction of 3-nitrocoumarins with vinyl ethers were converted in water into chromanols and tetrahydrofuro- and tetrahydropyrano-chromenes, we hypothesized that 3-nitrocoumarins could be converted, in an aqueous medium, into benzofurans. If this transformation is preceded by their Diels−Alder reaction with 1,3-dienes, dihydrodibenzo[*b,d*]furans could be prepared starting from 3-nitrocoumarins by carrying out the following reaction sequence in water: Diels−Alder/hydrolysis/decarboxylation/Nef/cyclodehydration. Considering that the synthesis in water of 3-nitrocoumarins was developed in this laboratory[5a,6e] via one-pot consecutive Knoevenagel−Pinner reactions between *o*-hydroxybenzaldehydes and nitroacetonitrile, dihydrod-ibenzo[*b,d*]furans can be prepared by a sequence of reactions carried out in water starting from suitably functionalized salicilaldehydes.

Here we report the use of 3-nitrocoumarins as 2π components in [4 + 2] cycloadditions with 1,3-dienes carried out in water, under solventless conditions, and in organic solvent for comparison to give nitrotetrahy-drobenzo[*c*]chromenones and their conversion to dihy-drodibenzo[*b,d*]furans in water. These latter compounds are practically unknown in the literature. To our knowl-edge, only two examples in the course of a cathodic electroreduction of dibenzofurans have been reported.[12]

Results and Discussion

3-Nitrocoumarin (**1a**) was used to study its conversion into benzofuran. NaBH$_4$ reduction of **1a** in water at room temperature gave 3-nitrochroman-2-one (**2**) very quickly with a 75% yield, which, under strong basic conditions (NaOH 3 M), hydrolyzed and decarboxylated affording nitrophenol **3** (Scheme 1). This product was then isolated in 98% yield by acidifying the alkaline reaction mixture. Quickly pouring the sodium salt of **3** into an ice-cooled 4.6 M H$_2$SO$_4$ aqueous solution (Nef conditions) allowed the isolation of the 1-benzofuran (**4**) in 68% yield.

The behavior of 3-nitrocoumarins **1a**−**c**, **5**, and **6** as 2π components in the Diels−Alder reactions with 1,3-butadienes **7**−**11** and cyclopentadiene (**12**) (Scheme 1) was then investigated in water, under solventless conditions, and in organic solvent.

In water, the cycloadditions of **1a** with **7**−**9** occurred under heterogeneous conditions and were faster (90 °C, 3 h) than when carried out in a homogeneous toluene solution (90 °C, 21−30 h) (Table 1, entries 1−6). With cyclopentadiene (**12**), the Diels−Alder reaction occurred at a lower temperature but the reactivity was the same in both aqueous and organic media (Table 1, entries 14, 15). High yields were always observed. The presence of the nitro group strongly increased the dienophilicity of the double bond of the coumarin moiety. Coumarin failed to react with 1,3-butadiene and isoprene (**8**) but reacted with 2,3-dimethyl-1,3-butadiene (**9**) under severe conditions with a low yield (260 °C, 40 h, 22%).[13]

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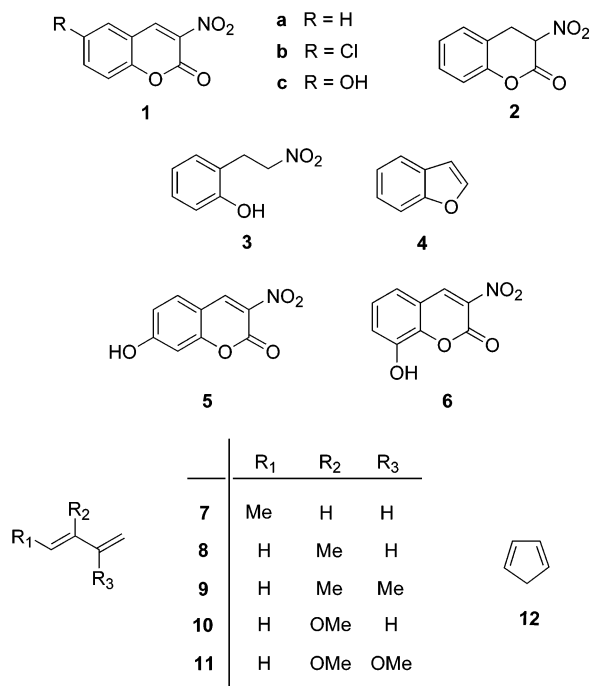
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SCHEME 1

TABLE 1. Diels–Alder Reactions of 3-Nitrocoumarin (1a)

entry	1,3-diene[a]	medium	T (°C)	time (h)	adducts (%)	yield (%)[b]
1	**7**	H_2O	90	3	**15a** (71), **16a** (23), **17** (6)	81
2	**7**	PhMe	90	30	**15a** (71), **16a** (23), **17** (6)	80
3	**8**	H_2O	90	3	**14a**	82
4	**8**	PhMe	90	24	**14a**	79
5	**9**	H_2O	90	3	**13a**	80
6	**9**	PhMe	90	21	**13a**	80
7	**10**[c]	H_2O	20	1.5	**24**	82
8	**10**	PhMe	20	218		
9	**10**	DCE	20	150	**24**	83
10	**11**[c]	H_2O	20	1	**20** (85), **21** (15)	85
11	**11**	PhMe	20[d]	24		
12	**11**	DCE	20	168	**23**	80
13	**11**	DCE	90	6	**23**	80
14	**12**	H_2O	30	3	**18a**	95
15	**12**	PhMe	30	3	**18a**	95

[a] Performed with 3 mol equiv. [b] Yield of isolated products. [c] In aqueous $NaHCO_3$ (pH 8.3). [d] At 90 °C, a complex mixture of unidentified compounds was found.

The cycloadditions of **1a** with 2,3-dimethyl-1,3-butadiene (**9**), isoprene (**8**), and cyclopentadiene (**12**) each gave only one product: **13a**, **14a**, and **18a**, respectively. The stereochemistry of **18a** indicates that the exo addition is exclusive. The observed diasteroselectivity can be rationalized considering that the secondary orbital interactions, originating from the exo approach, between 1,3-diene and nitro group lead to a greater stabilization than that originating from 1,3-diene and carbonyl group interactions in the endo approach.

When 3-nitrocoumarin (**1a**) behaves as a 4π component in [4 + 2] cycloaddition reactions with vinyl ethers, the stereochemistry of the addition is reversed: the secondary orbital interactions between the oxygen of the dienophile and the nitro group of 1,3-diene strongly favor the endo approach.[6a,e] The cycloaddition of **1a** with (*E*)-piperylene (**7**) in water was regioselective but not diastereoselective and gave a mixture of exo adduct **15a** (71%), endo adduct **16a** (23%), and the constitutional isomer **17** (6%) (Table 1, entry 1). A prolonged reaction time in toluene (90 °C, 30 h) gave the same result, showing that the reaction is under kinetic control. The lower diasteroselectivity observed can be ascribed to the steric interaction between the methyl group of (*E*)-piperylene and the nitro group that reduces the energetic gap between exo/endo approaches. No improvement of the diastereoselectivity was observed by performing the reaction at lower temperature.[14]

The results of the reaction of **1a** with 2,3-dimethoxy-1,3-butadiene (**11**) were surprising. In aqueous $NaHCO_3$ (pH 8.3),[15] the reaction was very fast at 20 °C and the nitrochromanones **20** and **21** were isolated in an 85/15 ratio and 85% yield (Table 1 entry 10). In toluene at room temperature, the reaction did not work, and at 90 °C, a complex mixture of unidentified compounds was found (Table 1, entry 11). In dichloroethane (DCE), on the contrary, the expected Diels–Alder adduct **23** was present as the sole reaction product at 20 °C and at 90 °C and was isolated in 80% yield (Table 1, entries 12 and 13). To explain these results, the reaction of **1a** with 2-methoxy-1,3-butadiene (**10**) was also carried out. In water alone or in DCE, the expected Diels–Alder adduct **24** was always the sole reaction product isolated in high yield (Table 1, entries 7 and 9), while the reaction did not work in toluene (Table 1, entry 8).

The results of our previous work[6e] suggest that 3-nitrocoumarin (**1a**) reacts with **11** as a 4π component and that **20** and **21** were the products of hydrolysis of the hypothetical nitronate **22**. The Diels–Alder adduct **22** was produced endo selectively, and therefore **20** and **21** originated from an unstereoselective generation of the stereogenic carbon bonded to the nitrogen atom in the course of hydrolysis, rather than from an unstereoselective [4 + 2] cycloaddition.

The results of the reactions of **1a** with **10** and **11** can be explained assuming that, in water, **11** assumes a s-transoid conformation (or a nonplanar s-cisoid conformation) because of the solvatation of the methoxy groups by water, which precludes in this way the behavior as a 1,3-diene and favors its reactivity as a vinyl ether. The solvatation does not greatly influence the s-cisoid–s-transoid conformational equilibrium of either **11** in DCE or **10** in water, and therefore **1a** gives the *normal* electron-demand Diels–Alder reaction with these 1,3-dienes in DCE and in water, respectively.

The cycloadditions of 6-chloro-3-nitrocoumarin (**1b**) with methyl-1,3-butadienes **7**–**9** and cyclopentadiene **12** were carried out in water. The results (Table 2) were substantially similar to those obtained with 3-nitrocoumarin (**1a**). The main differences were found in the reaction with (*E*)-piperylene (**7**) that only gave the two

(14) At room temperature no conversion at all was observed after 48 h, while at 50 °C after 24 h, 43 and 71% conversions were obtained in toluene and water, respectively. In both cases, no improvement on the diastereoselectivity was observed.

(15) An aqueous solution of $NaHCO_3$ at pH 8.3 was used in the cycloadditions with 2-methoxy- and 2,3-dimethoxy-1,3-butadiene because, under these conditions, the hydrolysis of dienes is strongly reduced.

TABLE 2. Diels-Alder Reactions of Substituted-3-nitrocoumarins

entry	reagents[a]	medium	T (°C)	time (h)	adducts (%)	yield (%)[b]
1	**1b, 7**	H_2O	90	5	**15b** (75), **16b** (25)	63
2	**1b, 8**	H_2O	90	5	**14b**	74
3	**1b, 9**	H_2O	90	2	**13b**	74
4	**1b, 12**	H_2O	30	1	**18b**(85), **19** (15)	90
5	**1c, 9**[c]	neat	150	2	**13c**	66
6	**5, 9**[c]	neat	150	2	**25**	55
7	**6, 9**[c]	neat	150	2	**26**	74

[a] Performed with 3 molar equiv of 1,3-diene. [b] Yield of isolated products. [c] Performed with 4 molar equiv of 1,3-diene.

diastereoisomers **15b** and **16b** (Table 2, entry 1) and in the reaction with cyclopentadiene (**12**) that also gave a 15% yield of endo adduct **19** (Table 2, entry 4). The cycloadditions of **1b** with 1,3-dienes **8** and **9** imitated those of **1a** with the same 1,3-dienes and only gave products **14b** and **13b**, respectively (Table 2, entries 2 and 3).
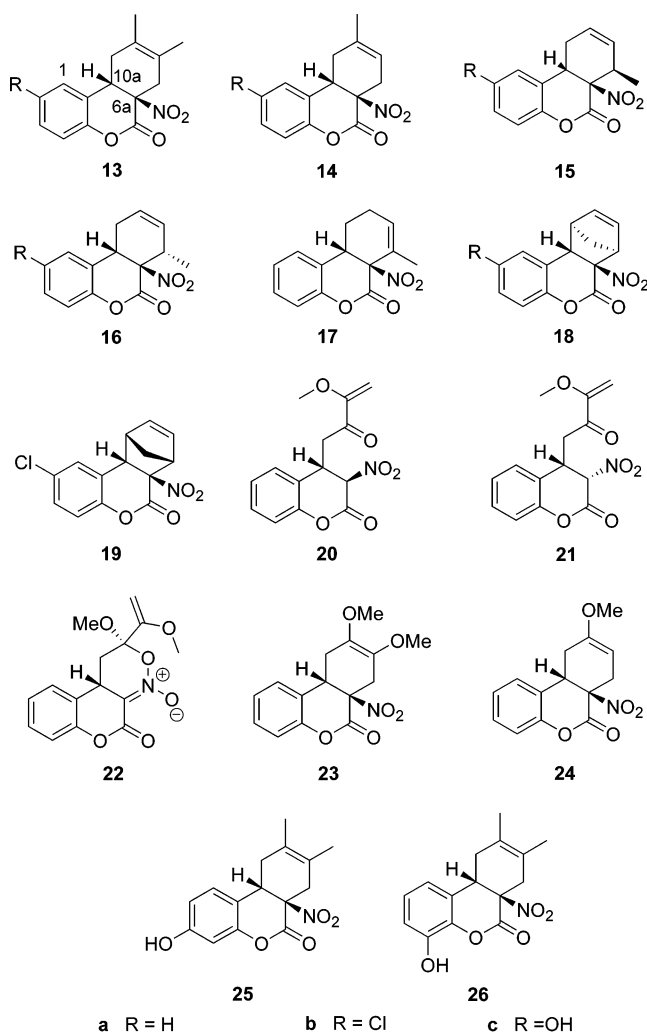
The preparation of nitrotetrahydrobenzo[c]chrome-nones **13−19** opens the route to the synthesis of conformationally constrained α-amino acid derivatives, which have applications in biological chemistry as enzyme inhibitors and peptidomimetics.[16]

The Diels−Alder reactions of hydroxy-3-nitrocoumarins **1c**, **5**, and **6** with **9** did not work in either water, toluene, or DCE we were able to carry out these processes working under solventless conditions at 150 °C. The cycloadducts **13c**, **25**, and **26** were isolated with satisfactory yields (Table 2, entries 5−7).

The Diels−Alder adducts **13−16**, **24**, and **25** were then submitted to hydrolysis and subsequent decarboxylation reactions under strong basic conditions (NaOH 3 M) followed by in situ Nef-cyclodehydration reactions in acidic medium (H_2SO_4 3.75 M).

The hydrolysis and decarboxylation reactions of cycloadducts **13−16** were complete in 1 h at 50 °C in the presence of 0.2 molar equiv of cetyltrimethylammonium bromide (CTABr), and the subsequent Nef-cyclodehydration reactions were carried out for 5 min at 0 °C and 1 h at room temperature (Table 3, entries 1−6). The process was selective, and the overall yields were good considering that the process involved five reactions (hydrolysis (**A**), decarboxylation (**B**), Nef (**C**), cyclyzation (**D**), and dehydration (**E**); see Scheme 3). The rearrangement of analogous methoxy derivative **24** carried out under the same reaction conditions, was accompanied by the hydrolysis of the vinyl ether functionality and gave **30** (Table 3, entry 7). The hydrolysis of **25** was carried out at room temperature and did not require CTABr, while the Nef-cyclodehydration reactions were slower. Dibenzo-[b,d]furan **32** (33%), derived from the aromatization process, was recovered along with the dihydrodibenzo-[b,d]furan **31** (Table 3, entry 8).

Structure of Compounds. Compounds **2−4**, **13a−c**, **14a,b**, **15a,b**, **18a,b**, and **23−31** were isolated as pure compounds. Attempts to obtain pure **16a,b**, **17**, **20**, and **32** were unsuccessful, and their structures were assigned by using an enriched mixture. The configurations of all

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SCHEME 2

13   14   15

16   17   18

19   20   21

22   23   24
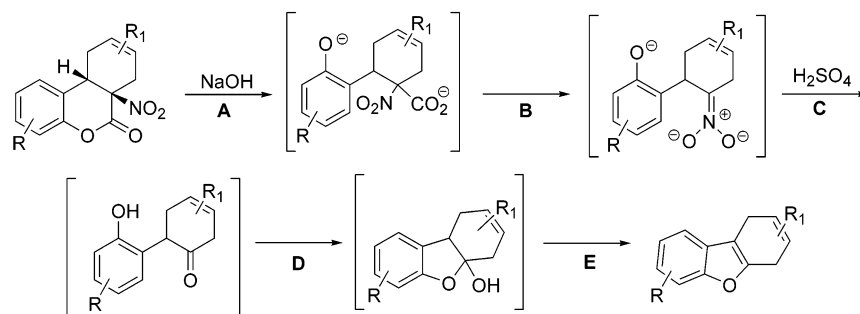
25   26

a R = H   b R = Cl   c R =OH

the compounds were assigned on the basis of their ^{1}H coupling constant values and NOE experiments. The data recorded for exo **15a** and **18a** are briefly discussed as examples.

The saturation of proton H_{10a} frequency in **15a** (δ = 3.85 ppm, J = 11.3, 7.0 Hz) gives a NOE effect on proton H_9 (6%), proton $H_{10\beta}$ (12%), and methyl protons (8%). The saturation of the methyl protons (δ = 1.09) frequency gives NOE effects, proton H_{10a} (10%) and proton H_8 (6%). The H_{10a}−$H_{10\alpha}$ and H_{10a}−$H_{10\beta}$ coupling constants values (11.3 and 7.0 Hz, respectively) show an axial−axial and an axial−equatorial relationship, respectively. The NOE effect of H_{10a} observed with proton $H_{10\beta}$ and the absence of a NOE effect between H_{10a} and proton $H_{10\alpha}$ suggest that proton H_{10a} occupies an axial position. The high NOE effect observed between proton H_{10a} and the methyl protons and with the very low NOE interaction with proton H_7 show a cis-1,3-diaxial relationship between the methyl group and H_{10a}.

NOE experiments did not help in clarifying the structure of cycloadduct **18a**. In a previous paper, we found that in structure-related compounds, the methano bridge is more shielded in the exo adducts (ca. 44 ppm) than the endo (ca. 48 ppm) adducts, giving a difference of ca. 4 ppm in the ^{13}C NMR analysis.[17] Accordingly, the ^{13}C methano bridge signals of compounds **18a** (44.6 ppm),

SCHEME 3

TABLE 3. Synthesis of Dihydrodibenzo[*b,d*]furans

Entry	Reagent	Reaction Conditions	Product	R	Yield (%)[a]
1	**13a**	b, c	**27**	H	48
2	**13b**	b, c	**27**	Cl	40
3	**14a**	b, c	**28**	H	49
4	**14b**	b, c	**28**	Cl	52
5	**15a + 16a**	b, c	**29**	H	50
6	**15b + 16b**	b, c	**29**	Cl	47
7	**24**	b, c	**30**		20
8	**25**	d, e	**31** 67% / **32** 33%		60

[a] Yield of isolated compounds. [b] Conditions: CTABr (0.2 molar equiv), 3 M NaOH, 50 °C, 1 h. [c] Conditions: 3.75 M H$_2$SO$_4$, 0 °C for 5 min, rt for 1 h. [d] Conditions: 3 M NaOH, rt, 1 h. [e] Conditions: 3.75 M H$_2$SO$_4$, 0 °C for 5 min, rt for 10 h.

18b (44.9 ppm), and **19** (48.9 ppm) are in agreement with the structures reported in Scheme 2.[17]

Conclusions

3-Nitrocoumarin (**1a**), 6-chloro-3-nitrocoumarin (**1b**), and hydroxy 3-nitrocoumarins **1c**, **5**, and **6** behaved as 2π components in the cycloaddition reaction with methyl-1,3-butadienes **7−9**, 2-methoxy-1,3-butadiene (**10**), and cyclopentadiene (**12**), while **1a** reacted as a 4π component in the [4 + 2] cycloaddition with 2,3-dimethoxy-1,3-butadiene (**11**) in water. The reactions of **1a** carried out in water under heterogeneous conditions were faster than those performed in toluene and DCE solution. Hydroxy-

(17) Angell, E. C.; Fringuelli, F.; Guo, M.; Minuti, L.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1988**, *53*, 4325−4328.

3-nitrocoumarins **1c**, **5**, and **6** only gave the Diels−Alder adducts when the reaction was carried out under solventless conditions. The nitrotetrahydrobenzo[*c*]chromenes originating from *normal* electron-demand Diels−Alder reactions were converted into 1,4-dihydrodibenzo[*b,d*]-furans and their analogues in generally satisfactory overall yields, by one-pot consecutive Nef-cyclodehydration reactions carried out in water.

Experimental Section

Representative Protocol for the Diels−Alder Reaction of 3-Nitrocoumarins 1a,b with 1,3-Butadienes 7−9 in Water: Rel(6a*R*,10a*S*)-8,9-Dimethyl-6a-nitro-6a,7,10,10a-tetrahydro-6*H*-benzo[*c*]chromen-6-one (13a). 3-Nitrocoumarin (**1a**) (0.382 g, 2.0 mmol), 10 mL of deionized water, and 2,3-dimethyl-1,3-butadiene **9** (0.493 g, 6.0 mmol) were added into a 14 mL metal reactor, sealed, and left under stirring at 90 °C for 3 h. The reaction mixture was extracted with ethyl acetate, and the combined organic layers were dried (Na$_2$SO$_4$) and evaporated under reduced pressure. The solid obtained was purified by column chromatography to give 0.437 g (80% yield) of the desired product **13a** as a white solid. Mp = 115−117 °C (*n*-hexanes−EtOH). ^{1}H NMR (200 MHz, CDCl$_3$) δ: 1.63 (s, 3H), 1.72 (s, 3H), 2.09 (dd broad, 1H, *J* = 17.8, 10.7 Hz), 2.50 (dd broad, 1H, *J* = 17.8, 6.8 Hz), 2.85 (d broad, 1H, *J* = 16.6 Hz), 3.18 (d broad, 1H, *J* = 16.6 Hz), 3.88 (dd, 1H, *J* = 10.7, 6.8 Hz), 7.05−7.38 (m, 4H); ^{13}C NMR (50.3 MHz, CDCl$_3$). ^{13}C NMR δ: 18.2, 18.4, 35.9, 36.4, 39.5, 90.8, 117.3, 122.1, 123.1, 123.8, 125.5, 127.7, 129.5, 149.8, 160.6. IR (CHCl$_3$) ν (cm^{-1}): 1780 (bs), 1555 (s), 1365 (s). MS *m/z* (relative intensity): 228 (23), 227 (100), 211 (87), 165 (35), 152, (23), 115 (27), 77 (22). Anal. Calcd for C$_{15}$H$_{15}$NO$_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.81; H, 5.53; N, 5.09.

Representative Protocol for the Reaction between 3-Nitrocoumarin (1a) and 1,3-Butadienes 10 and 11 in Water: Rel(6a*R*,10a*S*)-9-Methoxy-6a-nitro-6a,7,10,10a-tetrahydro-6*H*-benzo[*c*]chromen-6-one (24). 3-Nitrocoumarin (**1a**) (0.382 g, 2.0 mmol), NaHCO$_3$ (0.420 g, 5.0 mmol), and 10 mL of deionized water were added into a 15 mL flask, and the brown mixture was stirred at room temperature for 5 min. 2-Methoxy-1,3-butadiene (**10**) (0.505 g, 6.0 mmol) was added dropwise over a period of 5 min and the reaction mixture stirred for 1.5 h. The homogeneous mixture was transferred into a 50 mL separatory funnel and extracted with ethyl acetate, and the combined organic layers were dried (Na$_2$SO$_4$) and evaporated under reduced pressure. The product was purified by column chromatography (silica gel, ethyl acetate) to give 0.501 g (82% yield) of **24** as a white solid. Mp = 157−158 °C (petroleum ether−ethyl acetate). ^{1}H NMR (200 MHz, CDCl$_3$) δ: 2.27 (dd broad, 1H, *J* = 18.0, 10.2 Hz), 2.61 (dd broad, 1H, *J* = 18.0, 6.6 Hz), 3.00 (d broad, 1H, *J* = 16.8 Hz), 3.33 (dd broad, 1H, *J* = 16.8, 5.2 Hz), 3.52 (s, 3H), 4.07 (dd, *J* = 6.8, 10.4 Hz, 1H), 4.58−4.62 (m, 1H), 7.10−7.34 (m, 4H). ^{13}C NMR (100.6 MHz, CD$_3$COCD$_3$) δ: 29.2, 31.0, 38.9, 53.6, 88.5, 90.1, 117.4, 122.9, 125.6, 127.4, 129.8, 149.7, 151.3, 160.5.

Anal. Calcd for $C_{14}H_{13}NO_5$: C, 61.09; H, 4.76; N, 5.09. Found: C, 61.15; H, 4.82; N, 5.02.

Representative Nef-cyclodehydration Protocol for the Synthesis of Dihydrodibenzo[b,d]furans 27−31: 2,3-Dimethyl-1,4-dihydrodibenzo[b,d]furan (27a). To a 50 mL flask were added CTABr (0.147 g, 0.4 mmol), NaOH (3.6 g, 90 mmol), and 30 mL of water, and the resulting solution was warmed to 50 °C. The Diels−Alder adduct **13a** (0.546 g, 2.0 mmol) was added rapidly to the alkaline solution and left under stirring for 1 h. The final orange mixture was cooled to 0 °C and added dropwise to 15 mL of a 3.75 M H_2SO_4 solution previously transferred into a 100 mL flask and cooled (0 °C). The heterogeneous mixture was left under stirring at this temperature for 5 min and then left to warm to room temperature for 1 h. The mixture was transferred into a 250 mL separatory funnel, saturated with NaCl, and extracted with ethyl acetate, and the combined organic layers were dried (Na_2SO_4) and evaporated under reduced pressure. The gummy solid obtained was purified by column chromatography to give 0.190 g (48%) of the desired dihydrodibenzo[b,d]furan **27a** as a white solid. Mp = 91−93 °C (petroleum ether). ^1H NMR (200 MHz, $CDCl_3$) δ: 1.82 (s, 6H), 3.28 (m, 4H), 7.12−7.50 (m, 4H). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 18.9, 19.3, 29.8, 30.8, 110.5, 110.8, 118.5, 122.1, 122.2, 123.0, 123.8, 127.9, 151.7, 154.5. MS m/z (relative intensity): 198 (M^+, 68), 183 (100), 168 (37), 152 (12), 115 (10), 91 (11), 77 (5). Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.79; H, 7.12.

Supporting Information Available: General experimental procedures and spectral data for compounds **2**, **13−21**, **23−26** and **27−32**. This material is available free of charge via the Internet at http://pubs.acs.org.

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