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Reactions of Some Conjugated Dienes With an o-Quinone Monoimide≠

Harold W. Heine*, Wayne C. Schairer, Joseph A. Suriano
Department of Chemistry, Bucknell University, Lewisburg, Pennsylvania 17837

and

Elizabeth A. Williams*
General Electric Company, Corporate Research and Development
Schenectady, New York 12309

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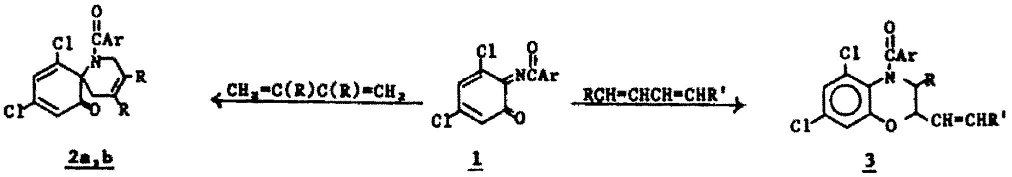
Abstract: The reactions of N-(2,4-dichloro-6-oxo-2,4-cyclohexadien-1-ylidene)-4-nitrobenzamide (1) with various conjugated dienes have been studied. The heterodiene system of 1 reacts with one of the double bonds of E-1,3-pentadiene, E,E-2,4-hexadiene, E,E-1,4-diphenyl-1,3-butadiene, E,E-2,4-hexadienal, ethyl sorbate, 1-methoxy-1,3-butadiene, cyclopentadiene, 1,2,3,4-tetraphenylcyclopentadiene in an inverse electron-demand Diels-Alder reaction to give derivatives of 2,3-dihydro-1,4-benzoxazines. In contrast to the above dienes 1,3-butadiene adds across the N-acylimino group of 1 to give the spiro adduct 2b.

Recently we observed that the diene system of 2,3-dimethyl-1,3-butadiene adds across the N-acylimino group of the o-quinone monoimide 1 to form the spiro adduct 2a (Scheme I)[1]. We now report the reactions of terminally substituted conjugated dienes (RCH=CHCH=CHR') with 1. In these reactions it is the heterodiene system of 1 that adds across one of the double bonds of the diene in an inverse electron-demand Diels-Alder reaction. The products are derivatives of 2,3-dihydro-1,4-benzoxazines 3 (Scheme I). Also described herein are the cycloaddition reactions of 1 with 1,3-butadiene, cyclopentadiene and 1,2,3,4-tetraphenyl-1,3-cyclopentadiene.

Scheme I



2a: R=Me; 2b: R=H

Ar=p-$O_2NC_6H_4$

Results and Discussion

Compound 1 reacts with 1,3-butadiene to give the spiro adduct 2b. The structure of 2b was established by X-ray crystallography and by ^{13}C NMR spectroscopy. Reaction of E,E-2,4-hexadiene (4) and 1 in methylene chloride did not form a spiro adduct but instead the 2,3-dihydro-1,4-benzoxazine 5 (97%) (Scheme II). An X-ray study on a crystal of 5 confirms that the configuration of the starting diene reagent 4 was maintained in the cycloadduct. Reaction of 1 with E-1,3-pentadiene proceeds analogously to give 6. That the terminal methylene group of the 1,3-pentadiene adds to the nitrogen of 1 is evident from the ^{13}C NMR spectrum of 6. Thus, the chemical shifts of the methyl group bonded to the olefinic carbon as well as the chemical shifts of the olefinic carbons of 6 are identical to the corresponding carbons of 5. Furthermore a signal at 47.63 ppm (CH_2 by off-resonance decoupling) is indicative of a methylene carbon attached to the nitrogen atom of 2,3-dihydro-1,4-benzoxazines[1]. The cycloadduct 7 is produced when 1 is treated with E,E-1,4-diphenyl-1,3-butadiene and the adduct 8a is formed in 74% yield when 1 and E,E-2,4-hexadienal are mixed in methylene chloride and the reaction mixture is kept at ambient temperature for seven days (Scheme II). An

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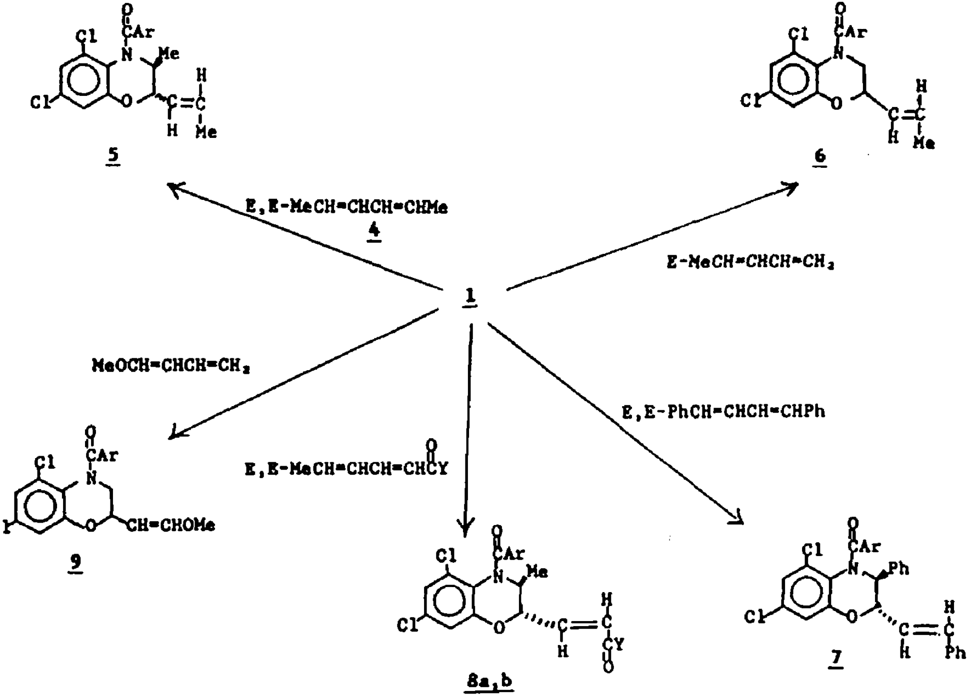
≠Dedicated to Professor Edward Taylor on the occasion of his 65th birthday.

X-ray crystallographic study of a single crystal of 8a shows that the heterodiene system of 1 adds across the terminal double bond of the dienal and that the stereochemistry of the dienal is maintained in the cycloadduct. Ethyl sorbate combines with 1 under similar conditions to produce 8b. Compound 1 and 1-methoxy-1,3-butadiene react instanteously, as was evident by the immediate disappearance of the bright orange color of 1, to give 9. The structure of 9 was proved by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of 9 exhibits intense peaks at 97 ppm and 154 ppm. The chemical shifts and intensities of these signals are typical of olefinic carbons which are protonated and which bear an electronegative substituent on one of the carbons. Another signal at 46.60 ppm (CH_2 by off-resonance decoupling) indicates, as mentioned previously, a methylene carbon linked to a nitrogen atom of 2,3-dihydro-1,4-benzoxazine.

Scheme II

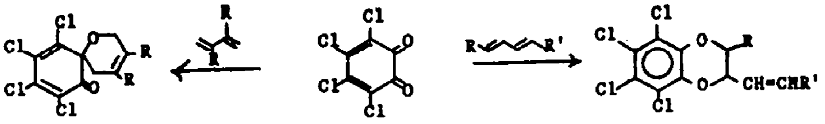


8a: Y=H; 8b: Y=OEt

Steric factors appear to be responsible for whether reactions of 1 with conjugated dienes lead to the spiro adducts 2a,b or to the 2,3-dihydro-1,4-benzoxazines 5-9. In the case of the 1,3-butadiene and 2,3-dimethyl-1,3-butadiene, where the terminal carbons are unsubstituted and relatively unhindered, addition of the diene system takes place across the highly substituted imino group of 1 to afford 2a-b. Terminally substituted dienes like E-1,3-pentadiene, E,E-2,4-hexadiene, E,E-2,4-hexadienal, etc. are too bulky to interact with the imino group of 1. In such instances the electron-deficient heterodiene system of 1 adds to the most electron-rich double bond of the diene resulting in the formation of 5-9.

Steric influences appear to be operative, too, in the reactions of o-chloranil (10) with terminally substituted 1,3-dienes. With 2,3-dimethyl-1,3-butadiene and 2,3-diphenyl-1,3-butadiene where the terminal carbons are bonded only to hydrogen, the diene system adds to the carbonyl group to give the spiro adducts 11a,b (Scheme III). With the more sterically demanding 1-aryl-1,3-butadienes and 2,4-hexadiene the heterodiene moiety of 10 combines with one of the double bonds of the diene to form the dioxins 12a,b.[2]

Scheme III



11a,b

11a: R=Me

11b: R=Ph

10

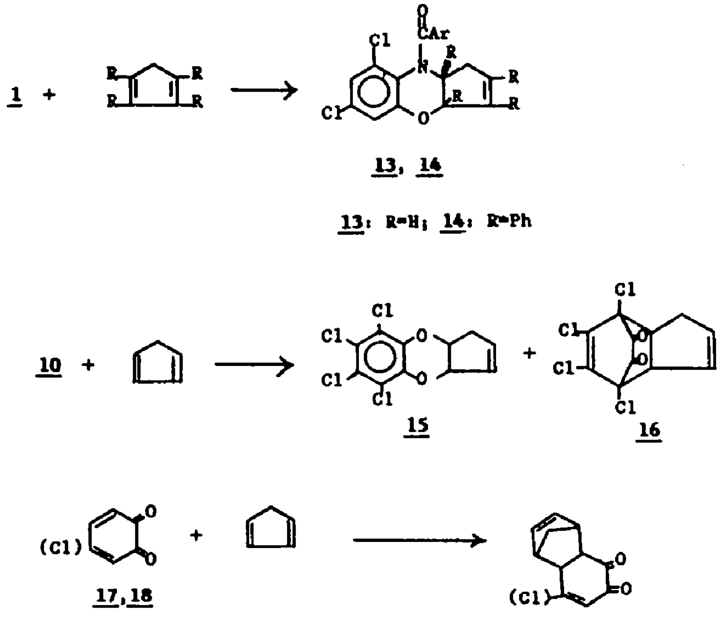
12a,b

12a: R=H, R'=Ph

12b: R=R'=Me

Cyclopentadiene and 1,2,3,4-tetraphenyl-1,3-cyclopentadiene act as dienophiles towards the heterodiene system of **1**. In each instance it is the C-1 carbon of the cyclic diene that bonds to the electrophilic nitrogen of **1** to give the adducts **13** and **14** respectively (Scheme IV). The structures of **13**, **14** were determined by X-ray crystallography on single crystals. It has been reported that heating a benzene solution of cyclopentadiene and o-chloranil (**10**) gives a mixture of the adducts **15** (64%) and **16** (23%)$^{3-5}$ (Scheme IV). In the formation of **15** and **16** the cyclopentadiene is the electron-rich dienophilic component for both the heterodiene and the homodiene functionalities of **10**. With the less hindered and less electrophilic o-quinone (**17**) and 4-chloro-o-quinone (**18**) the cyclopentadiene acts as the diene component of the Diels-Alder reaction and adds across one of the double bonds of the homodiene to form the adducts **19** and **20**. There was no evidence of either the homodiene system or one of the double bonds of **1** interacting with cyclopentadiene to produce adducts similar to **16**, **19** or **20**. Presumably the N-p-nitrobenzoylimino group of **1** renders the heterodiene system so electrophilic that cycloadditions at other sites are precluded.

Scheme IV



13, **14**

13: R=H; **14**: R=Ph

15

16

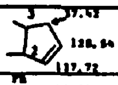
17,**18**

19,**20**

Experimental

NMR Spectra: Carbon-13 NMR spectra were obtained on a Varian XL-300 NMR spectrometer operating at 75.4 MHz for carbon. All spectra were obtained with complete proton decoupling except when off-resonance decoupling experiments were performed to determine carbon multiplicities. Typical spectral parameters include a 20 kHz spectral width, 32K data points, 12 μs pulse width corresponding to a 45° flip angle, and 2s pulse delay. The spectra of several of the 2,3-dihydro-1,4-benzoxazine derivatives were obtained at high temperatures (80-120°C) to equilibrate ring inversion and amide isomers. The ^{13}C NMR chemical shifts for compounds 5-9 and 13-14 are shown in Table I.

Table I. Carbon-13 NMR Chemical Shifts[a] for Compounds 5-9 and 13-14

	R_1	R_2	2	3	4a	5	6	7	8	8a	9	10	11	12	13
5	CH_3 (16.21)	$CH=CHCH_3$ (127.18; 130.18; 17.10)	80.97	51.96	∅	∅	123.15	132.31	115.77	149.38	167.24	141.13	128.90	123.12	148.74
6	H	$CH=CHCH_3$ (125.92; 131.61; 17.52)	77.38	47.65	122.88	∅	121.85	132.40	116.29	149.45	167.19	140.45	129.33	123.26	149.16
7	Ph	$CH=CHPh$ (∅; (136.12) (131.65))	78.86 78.47	53.78 53.43	∅	131.92	122.78 122.91	132.69 132.78	116.32 116.06	149.03 149.04	169.53 167.49	140.61 141.06	∅	(124.62) (123.60)	148.90 148.72
8	CH_3 (16.69 16.66)	$CH=CHCHO$ (151.79 149.37; 132.18 131.98; 133.17 133.68)	79.27 77.96	46.35 51.04	120.31 118.05	129.49 131.42	122.97	132.95 132.50	115.97 115.72	(under 148.37) 149.23	168.30 166.02	140.06 138.74	128.76 128.16	123.16 124.33	147.88 146.56
9	H	$CH=CHOMe$ (97.61 97.13; 153.91; 56.80)	76.02 78.35	50.94 46.63	121.93 122.02	130.03 131.96	120.51 121.06	132.25 132.77	115.28 115.76	150.57 150.12	168.73 166.63	139.70 141.51	130.47 131.67	124.14 123.41	148.83 148.86
13			80.79	57.92	127.25	129.64	123.95	133.35	119.14	152.82	166.60	140.94	129.39	122.91	148.82
14			82.68	63.75	126.03	130.47	∅	132.67	119.44	149.68	167.32	141.78	130.03	122.77	148.74

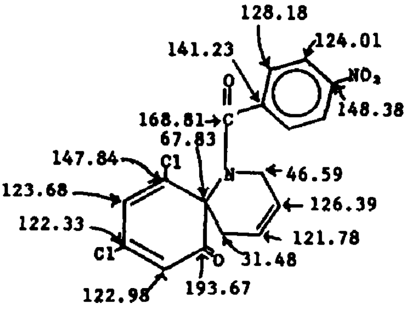
∅ buried

() values in parentheses are tentative

[a] Chemical shifts in $CDCl_3$ or $(CDCl_2)_2$. Compounds with two values for each carbon were run at -30°C; peaks arise from isomerism about amide linkage.

9,11-Dichloro-3,4-dimethyl-1-(4-nitrobenzoyl)-1-azaspiro-[5.5]-undeca-3,8,10-trien-7-one (2b). A 3 dram vial containing 175 mg (0.54 mmol) of 1 in 5 mL of CH_2Cl_2 was placed in an ice bath. Approximately 2.0 g of 1,3-butadiene was introduced into the solution and the vial was wired shut. The reaction mixture was kept at ambient temperature for 1 hr, and then the solvent was evaporated. The residue was slurried with MeOH and then filtered to give 19.0 mg (93%) of crude 2b. Three recrystallizations from methanol gave an analytical sample melting at 163-164°C (molecular ion m/e 378). Anal. Calcd. for $C_{17}H_{12}Cl_2N_2O_4$: C, 53.85; H, 3.19; N, 7.38. Found: C, 53.95; H, 3.59; N, 7.44.

The natural abundance ^{13}C NMR spectrum of 2b is summarized in the following structure:



2b

[2S-[2α(E),3β]]-5,7-dichloro-3,4-dihydro-3-methyl-4-(4-nitrobenzoyl)-2-(1-propenyl)-2H-1,4-benzoxazine (5). To a stirred solution of 58 mg (0.70 mmol) of *trans,trans*-2,4-hexadiene in 2.5 mL of CH_2Cl_2 was added 229 mg (0.70 mmol) of 1. The mixture was warmed briefly to dissolve all of the 1 and then kept at ambient temperature for 22 h. The solvent was evaporated, and the residue slurried with MeOH and filtered to give 275 mg (97%) of 5, mp 168-170°C; mass spectrum, m/e 406 (molecular ion). Anal. Calcd. for $C_{19}H_{16}N_2O_4Cl_2$: C, 56.04; H, 3.96; N, 6.88. Found: C, 55.93; H, 4.30; N, 6.78.

5,7-Dichloro-3,4-dihydro-4-(4-nitrobenzoyl)-2-E-(1-propenyl)-2H-1,4-benzoxazine (6). A mixture of 21 mg (0.31 mmol) of *trans* piperylene, 1 mL of CH_2Cl_2, and 102 mg (0.31 mmol) of 1 was allowed to stand at ambient temperature for 1 h. The solvent was evaporated and the residue was triturated with MeOH and filtered to give 118 mg (97%) of crude 6, mp 161-165°C. Recrystallization from EtOH afforded 6, mp 170-172°C: mass spectrum, m/e 392 (molecular ion). Anal. Calcd. for $C_{18}H_{14}Cl_2N_2O_4$: C, 54.98; H, 3.59; N, 7.12. Found: C, 55.06; H, 3.99; N, 7.15.

[2S-[2α(E),3β]]-5,7-dichloro-3,4-dihydro-3-phenyl-4-(4-nitrobenzoyl)-2-(2-phenylethenyl)-2H-1,4-benzoxazine (7). A mixture of 221 mg (0.68 mmol) of 1, 140 mg (0.68 mmol) of *trans,trans*-1,4-diphenyl-1,3-butadiene in 4 mL of CH_2Cl_2 was warmed briefly to dissolve the reactants. The solvent was evaporated after 18 h and MeOH was added to the residue. The white solid which formed was filtered. The crude 7 (278 mg, 77%) melted at 168-172°. Recrystallization from MeOH gave 11 melting at 169-171°; mass spectrum, m/e 539 (molecular ion). Anal. Calcd. for $C_{29}H_{20}Cl_2N_2O_4$: C, 65.55; H, 3.79; N, 5.27. Found: C, 65.26; H, 3.90; N, 5.34.

[2S-[2α(E),3β]]-5,7-dichloro-3,4-dihydro-3-methyl-4-(4-nitrobenzoyl)-2-(3-oxo-1-propenyl)-2H-1,4-benzoxazine (8a). To a solution of 72 mg (0.75 mmol) of *trans,trans*-2,4-hexadienal in 6.51 g of CH_2Cl_2 was added 249 mg (0.738) of 1. After the reaction mixture stood for 8 d at ambient temperature the solvent was evaporated and the residue triturated with ethanol. Filtration gave 230 mg (74%) of 8a melting at 186-187°C. Recrystallization from ethanol afforded crystals of 8a, mp 203-205°. Anal. Calcd. for $C_{19}H_{14}Cl_2N_2O_5$: C, 54.17; H, 3.35; N, 6.65. Found: C, 53.99; H, 3.59; N, 6.52.

Ethyl 3-[5,7-dichloro-3,4-dihydro-3-methyl-4-(4-nitrobenzoyl)-2H-1,4-benzoxazin-2-yl]-2-propenoate (8b). A mixture of 74 mg (0.53 mmol) of ethyl sorbate, 1.81 g CH_2Cl_2 and 171 mg (0.53 mmol) was allowed to stand 8 d at ambient temperature. Evaporation of the solvent, slurrying the residue with MeOH and filtering gave 212 mg (87%) of 8b, mp 163-165°C. Recrystallization from EtOH and then CH_3CN formed 12b, mp 166-168°C; mass spectrum, m/e 464 (molecular ion). Anal. Calcd. for $C_{21}H_{18}Cl_2N_2O_6$: C, 54.21; H, 3.89; N, 6.02. Found: C, 53.88; H, 3.94; N, 6.00.

5,7-Dichloro-3,4-dihydro-2-(2-methoxyethenyl)-4-(4-nitrobenzoyl)-2H-1,4-benzoxazine (9). To a solution of 83 mg (0.98 mmol) of 1-methoxy-1,3-butadiene in 3 mL of CH_2Cl_2 was added dropwise 320 mg (0.98 mmol) of 1. The reaction was exothermic. Within 30 s the color of the reaction mixture changed from orange to yellow. After 1 h the solvent was evaporated and 1 mL of MeOH was added with stirring. The white precipitate that formed was filtered to give 241 mg of 9, mp 158-163°C. The filtrate was concentrated and filtered to give an additional 139 mg of 9 mp 154-159°. The two fractions had the same retention time in the gas chromatograph. The total yield of 13 was 94%. Recrystallization from MeCN formed 13, mp 162-163°; mass spectrum, m/e 408 (molecular ion). Anal. Calcd. for $C_{18}H_{14}N_2O_5Cl_2$: C, 52.83; H, 3.45; N, 6.85. Found: C, 52.70; H, 3.40; N, 6.97.

(3aS-cis)-6,8-dichloro-1,3a,9,9a-tetrahydro-9-(4-nitrobenzoyl)-cyclopenta[b][1,4]benzoxazine (13). Into a vial containing 2.0 g of CH_2Cl_2 162 mg (0.5 mmol) of 1 was added 99 mg (1.5 mmol) of cyclopentadiene. The color of the reaction mixture changed from orange to yellow immediately. After 6 h the solvent was evaporated and the brown gummy residue slurried with methanol and filtered. The yield was quantitative and the crude 13 melted at 100-105°. Recrystallization from 1-propanol gave 13, mp 150-152°. Anal. Calcd. for $C_{18}H_{12}N_2O_4Cl_2$: C, 55.26; H, 3.09; N, 7.16. Found: C, 55.16; H, 3.25; N, 6.92.

(3aS-cis)-6,8-dichloro-1,3a,9,9a-tetrahydro-9-(4-nitrobenzoyl)-2,3,3a,9-tetraphenylcyclopenta[b][1,4]benzoxazine (14). To a solution of 74 mg of 1,2,3,4-tetraphenyl-1,3-cyclopentadiene in 3.84 g CH_2Cl_2 was added 66 mg of 1. The reaction mixture was initially a dark golden brown color but after 44 h at ambient temperature the color had changed to yellow. The solvent was evaporated, the residue slurried with a small amount of MeOH and filtered. The crude 14 weighed 122 mg (87%); discolored at 183° and melted at 193-198°. Recrystallization from MeOH gave 14, mp 211-215°. The infrared spectra of the crude and recrystallized 14 were identical. Anal. Calcd. for $C_{42}H_{28}Cl_2N_2O_4$: C, 72.52; H, 4.06; N, 4.03. Found: C, 72.46; H, 4.16, N, 4.05.

The atomic co-ordinates for compounds 2b, 5, 8a, 13 and 14 are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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1. Heine, H. W.; Barchiesi, B. J.; Williams, E. A. J. Org. Chem. **1984**, **49**, 2560.
2. Ansell, M. F.; Leslie, V. J. J. Chem. Soc. C **1971**, 1423.
3. Horspool, W. M.; Tedder, J. M.; Din, Z. U. Chem. Comm., **1966**, 775.
4. Horspool, W. M.; Tedder, J. M.; Din, Z. U. J. Chem. Soc. **1966**, 775.
5. Ansell, M. F.; Gosden, A. F.; Leslie, V. J.; Murray, R. A. J. Chem. Soc. C **1971**, 1401.