time the color of the thioenone faded. Following this, the unreacted acrylonitrile and benzene were distilled off under reduced pressure. GC analysis of the irradiated mixture revealed the presence of two products in addition to the oxidation product, the corresponding ketone. The crude irradiated mixture on washing with petroleum ether (60–80 °C) gave 175 mg of white solid which was collected by filtration and identified to be thietane **2a** by its spectral properties. The filtrate on evaporation of the solvent gave a residue which was then subjected to preparative TLC (silica gel–hexane/benzene). While the first zone afforded the unreacted thioenone 1 (80 mg), the second zone showed the presence of two compounds. Rechromatography of this fraction gave thietanes **2a** (25 mg) and **2b** (25 mg) in pure forms.

**Selective Excitation and Quenching Studies To Identify the Reactive State. (i) Selective Excitation to $S_1(n\pi^*)$.** Pyrex tubes containing benzene solutions (5 mL) of thioenone 1 (0.12 M) and various olefins (4.8 M) were purged with nitrogen for 20 min and sealed. These solutions were irradiated for about 15 days by using a 450-W medium pressure mercury arc lamp with Corning glass filter CS-3.67 (transmission above 540 nm). No reaction was detected either by visible absorption (OD at 600 nm) or $^1H$ NMR.

**(ii) Selective Excitation to $S_2(\pi\pi^*)$.** Pyrex tubes containing benzene solutions (5 mL) of thioenone 1 (0.01 M) and olefins (0.3 M) were purged with nitrogen for 20 min and irradiated by using a 450-W medium pressure mercury arc lamp with Corning glass filters CS-0.52 and CS-7.60 (transmission between 340 and 420 nm). The color of the solution faded within 3 h and at this stage solvent benzene and excess olefin were removed and the resultant mixture was analyzed by GC. GC analysis of the product mixture showed that the products formed upon selective excitation of thioenone 1 to the $\pi\pi^*$ state in the above manner are the same as those obtained upon irradiation using RPRp 350-nm lamps.

**(iii) Quenching Studies.** Quenching studies were carried out by using biacetyl ($E_{S_1} \simeq 65$ kcal mol$^{-1}$, $E_{T_1} \simeq 56$ kcal mol$^{-1}$) and naphthalene ($E_{S_1} \simeq 93$ kcal mol$^{-1}$, $E_{T_1} \simeq 61$ kcal mol$^{-1}$) as quenchers. The system chosen for detailed investigation was thioenone 1 and acrylonitrile. Six solutions containing fixed concentrations of thioenone (0.01 M) and acrylonitrile (0.2 M) and varying quencher concentrations (0.0–0.25 M) were made and deaerated by purging with nitrogen. The above solutions, sealed with rubber corks, were then irradiated in a merry-go-round style by using a 450-W medium pressure mercury lamp with Corning glass filters CS-0.52 and CS-7.60. The amounts of the thietanes formed after 3 h of irradiation (conversion: less than 20%) were then estimated by using an analytical GC, based on which, the relative quantum yields were calculated. The relative quantum yields for the above cycloaddition decreased with increasing biacetyl concentration but remained constant with increasing naphthalene concentration. Linear Stern–Volmer plots were obtained with positive and zero slopes for biacetyl and naphthalene quenchers, respectively. The lifetime estimated from the biacetyl quenching (assuming diffusion-controlled rate) is close to that obtained from triethylamine quenching of $S_2$ fluorescence.

**Fluorescence ($S_2$) Quenching by Olefins.** Fluorescence spectrum of thioenone 1 was recorded on a Shimadzu RF-540 spectrofluorimeter by setting the excitation wavelength at 400 nm. In a typical experiment, a 0.01 M solution of thioenone 1 was made in deaerated benzene and 3 mL of this was syringed into a quartz cell fitted with a Teflon stopcock. The solution was deaerated by passing dry $N_2$ for about 30 min. Fluorescence intensity of the solution was measured in the absence of the quencher and after the addition of aliquots of the olefin by setting all experimental conditions the same. The increase in volume of the solution was less than 5% even after the addition of the required amount of olefin to reach the highest quencher concentration. Intensities at the emission maximum were determined and these were utilized to obtain Stern–Volmer plots ($F_0/F$ vs concentration of the quencher). From these linear Stern–Volmer plots, $k_q$ for all the quencher olefins were estimated and these are summarized in Table II.

**Acknowledgment.** Financial support obtained from the Department of Science and Technology is duly appreciated. We also thank Dr. J. Chandrashekhar for his invaluable assistance during the MO calculations.

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# Metallic Nickel Assisted Room-Temperature Generation and Diels–Alder Chemistry of *o*-Xylylene Intermediates

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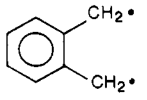
*Received June 1, 1987*

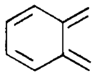
Highly reactive metallic nickel, prepared by the lithium metal reduction of nickel iodide using naphthalene as an electron carrier, was found to induce 1,4-dehalogenation of $\alpha,\alpha'$-dihalo-*o*-xylene derivatives at room temperature. The reaction proceeds in the presence of a variety of electron-deficient olefins, giving Diels–Alder cycloadducts in moderate to good yields presumably via the highly reactive intermediate *o*-xylylene 2. 1,3-Dibromoindan and 1,4-dibromo-1,2,3,4-tetrahydronaphthalene also react in the presence of electron-deficient olefins to give bridged cycloadducts in moderate yields. Methoxy as well as electron-deficient substituents such as bromide and nitrile groups on the aromatic ring of the starting dibromide were shown to be compatible with the reaction conditions yielding substituted cycloadducts in good yields.

## Introduction

The Diels–Alder reaction of various dienophiles with the highly reactive diene *o*-xylylene has been utilized extensively in the construction of various polycyclic ring systems. Although calculations show that the *o*-xylylene species may actually be best represented as biradicaloid 1,[1] its reactivity parallels that of a highly reactive diene 2. The high reactivity presumably results from attainment of aromaticity in the Diels–Alder cycloadduct.



1



2

A variety of methods have been employed to generate the *o*-xylylene intermediate.[2] Among them are ring

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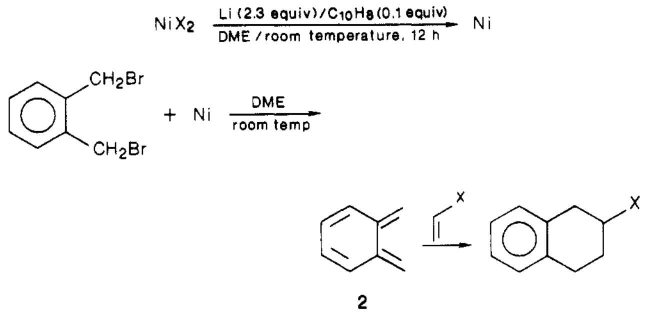
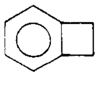
[1] Ichikawa, H.; Ebisawa, Y.; Honda, T.; Kametani, T. *Tetrahedron* **1985**, *41*, 3643.

0022-3263/88/1953-0339$01.50/0

**Scheme I**



openings of benzocyclobutenes 3[3] and various "extrusion" reactions involving loss of a small molecule from a cyclic system. For example, losses of $N_2$ from 4[4] or $SO_2$ from 5[5] have been shown to lead to the *o*-xylylene intermediate **2**.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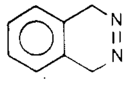

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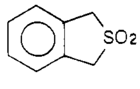


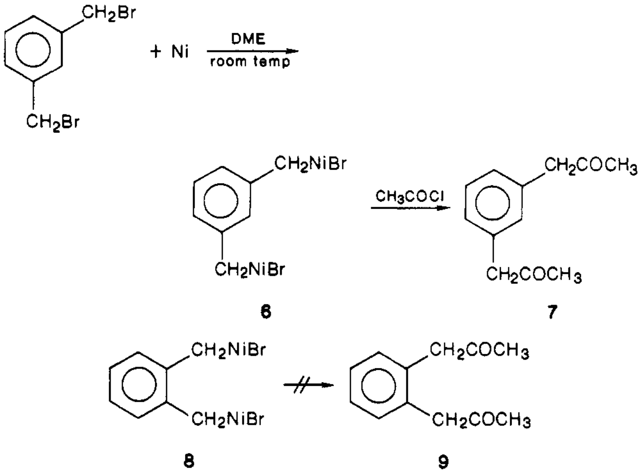
5

One of the more fundamental methods for generation of the *o*-xylylene intermediate is 1,4-elimination from *o*-xylene derivatives. *o*-Xylene di-, tri-, or tetrabromides undergo intramolecular 1,4-dehalogenation by means of sodium iodide,[6] lithium,[7] zinc,[8] copper,[9] iron,[10] and chromium.[11] Hofmann degradation of (*o*-methylbenzyl)trimethylammonium hydroxides,[12] as well as the more recently developed fluoride ion induced elimination from [*o*-[$\alpha$-(trimethylsilyl)alkyl]benzyl]trimethylammonium halides,[13] have also been effectively utilized in the generation of **2**.

In the course of our investigations concerning the scope of reactions of activated nickel with various organic substrates, we discovered that 1,4-dihalide eliminations from $\alpha,\alpha'$-dibromo-*o*-xylene derivatives were induced at room temperature with activated nickel, giving *o*-xylylene intermediates. Electron-withdrawing or -donating groups can be present in the starting *o*-xylene dihalides. The resultant *o*-xylylene intermediates were trapped with a variety of electron-deficient olefins, giving the Diels–Alder cycloadducts in moderate to good yields.

## Results and Discussion

**Scheme II**



Previous communications[14] have shown the high reactivity and utility of activated nickel powder, prepared by the lithium metal reduction of nickel iodide with a catalytic amount of naphthalene as an electron carrier in 1,2-dimethoxyethane (DME). The active nickel produced reacts readily under mild conditions with $\alpha,\alpha'$-dibromo- and $\alpha,\alpha'$-dichloro-*o*-xylene in the presence of electron-deficient olefins, yielding substituted 1,2,3,4-tetrahydronaphthalene (tetralin) derivatives in moderate to good yields (Scheme I). A plausible explanation for this process would invoke the *o*-xylylene intermediate **2**. Insertion of Ni into one of the carbon–halogen bonds, followed by rapid elimination of $NiBr_2$, would produce **2**. Whether the *o*-xylylene produced exists free in solution or is coordinated by Ni is uncertain.

A variety of electron-deficient olefins were shown to be effective dienophiles, giving the expected cycloaddition products (Table I). Reaction of the *o*-xylylene species **2** with maleic anhydride yielded only the cis product, while cis olefins (e.g. dimethyl or diethyl maleate) yielded a mixture of cis and trans cycloaddition products. Trans esters (diethyl fumarate and methyl crotonate) yielded trans adducts; however, fumaronitrile gave a mixture of cis and trans adducts. In a separate experiment, it was discovered that upon exposure to the activated nickel, dimethyl maleate was isomerized to dimethyl fumarate. The exact mechanism of the isomerization is at this point unexplained. Noncyclic cis olefins appear to give mixtures of cis and trans cycloadducts while trans olefins may yield trans products or mixtures of cis and trans products. In cases where mixtures are produced, the trans isomer is the major adduct isomer with the ratio of cis/trans isomers apparently being affected by the nature of the olefin. Thus, although the cycloaddition reaction itself is still not proven to be a "concerted" rather than a stepwise process, the mixture of cis and trans cycloadducts could arise from isomerization of the olefin prior to the cycloaddition process.

2-Cyclohexen-1-one, methyl vinyl ketone, phenylacetylene, diphenylacetylene, benzaldehyde, perfluoro-1-heptene, and cyclohexene were found to not be effective dienophiles for the reaction. Only polymeric *o*-xylylene products were seen in the reaction mixtures. In addition, no cycloadduct was produced by using *p*-benzoquinone as the dienophile. Only hydroquinone and $\alpha,\alpha'$-diiodo-*o*-xylene were recovered. The hydroquinone presumably results from the reduction of benzoquinone by nickel.

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(2) These topics are covered in two review articles: (a) McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270. (b) Oppolzer, W. *Synthesis* **1978**, *11*, 793.

(3) (a) Kametani, T.; Kato, Y.; Honda, T.; Fukimoto, K. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2001. (b) Fleming, I.; Gianni, F. L.; Mah, T. *Tetrahedron Lett.* **1976**, 881.

(4) Flynn, C. R.; Michl, J. *J. Am. Chem. Soc.* **1974**, *96*, 3280.

(5) (a) Cava, M. P.; Deana, A. A. *J. Am. Chem. Soc.* **1959**, *81*, 4266. (b) Sisido, K.; Noyori, R.; Nozaki, H. *J. Am. Chem. Soc.* **1962**, *84*, 3562. (c) Oppolzer, W.; Roberts, D. A.; Bird, T. G. *Helv. Chim. Acta* **1979**, *62*, 2017.

(6) (a) Cava, M. P.; Napier, D. R. *J. Am. Chem. Soc.* **1957**, *79*, 1701. (b) Cava, M. P.; Deana, A. A.; Muth, K. *J. Am. Chem. Soc.* **1959**, *81*, 6458.

(7) Avram, M.; Dinulescu, I. G.; Dinu, D.; Matescu, G.; Nenitzescu, C. D. *Tetrahedron* **1963**, *19*, 309.

(8) (a) Alder, K.; Fremery, M. *Tetrahedron* **1961**, *14*, 190. (b) Boudjouk, P.; Han, B. H. *J. Org. Chem.* **1982**, *47*, 751.

(9) Ito, Y.; Yonezawa, K.; Saegusa, T. *J. Org. Chem.* **1974**, *39*, 2769.

(10) (a) Sisido, K.; Kusano, N.; Noyori, R.; Nozaki, Y.; Simosaka, M.; Nozaki, H. *J. Polym. Sci., Ser. A* **1963**, *1*, 2101. (b) Nozaki, H.; Noyori, R. *Tetrahedron* **1966**, *22*, 2163.

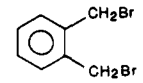
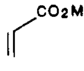
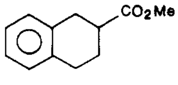
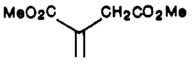
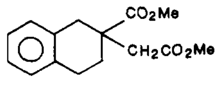
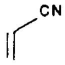
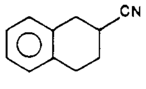
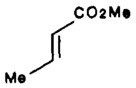
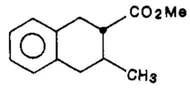
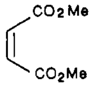
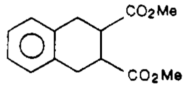
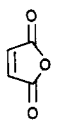
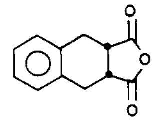
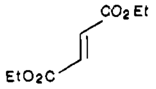
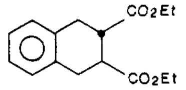
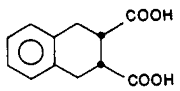
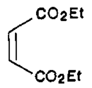
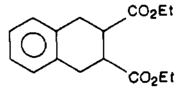
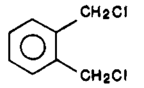
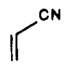
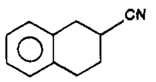
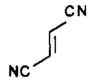
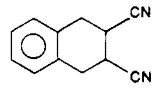
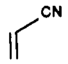
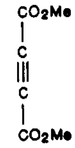
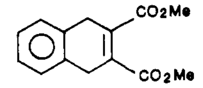
(11) Stephan, D.; Gorgues, A.; Le Coq, A. *Tetrahedron Lett.* **1984**, *25*, 5649.

(12) Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 949.

(13) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1982**, *104*, 7609.

(14) (a) Inaba, S.; Rieke, R. D. *J. Org. Chem.* **1985**, *50*, 1373. (b) Matsumoto, H.; Inaba, S.; Rieke, R. D. *J. Org. Chem.* **1983**, *48*, 840. (c) Inaba, S.; Matsumoto, H.; Rieke, R. D. *J. Org. Chem.* **1984**, *49*, 2093.

**Table I. Nickel-Mediated Cycloadditions of *o*-Xylylene with Dienophiles[a]**

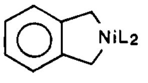
| starting dihalides | dienophiles (molar equiv)[c] | adducts (% isolated yield)[b] | starting dihalides | dienophiles (molar equiv)[c] | adducts (% isolated yield)[b] |
|---|---|---|---|---|---|
|  | <br>(2) | <br>**20** (67) |  | <br>(2) | <br>**29** (42) |
|  | <br>(2) | <br>*21* (67) |  | <br>(2) | <br>**30** (14)[e] |
|  | <br>(2) | <br>**22,23** (47)<br>(trans/cis = 2/1)[d] |  | <br>(2) | <br>**31** (7) |
|  | <br>(2) | <br>**24** (76) |  |  | <br>**32** (61) |
|  | <br>(2) | <br>**24,25** (90)<br>(trans/cis = 1/1)[d] |  | <br>(2) | <br>**33** (61) |
|  | <br>(2) | <br>**26,27** (54)<br>(trans/cis = 2/1)[d] |  | <br>(1) | **33** (63) |
|  | <br>(2) | <br>**28** (63) |  |  |  |

[a] All reactions were carried out at room temperature. [b] Isolated by silica gel chromatography. [c] Molar equivalents of dienophile are relative to starting dibromide. [d] Trans/cis ratio determined by GLPC analysis and by $^1$H NMR integration of crude products. [e] A small amount (<5%) of 1,2-bis(2-(iodomethyl)phenyl)ethane was also isolated.

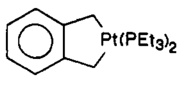
Since sodium iodide is known to react with dibromo-*o*-xylene to give diiodo-*o*-xylene,[15] the diiodo-*o*-xylene could result from the reaction of unconsumed dibromo-*o*-xylene with lithium iodide which is present in the reaction flask. These results are analogous to those reported in a similar reaction by Scheffer[16] where the use of zinc metal and ultrasound gave only hydroquinone and a quantitative yield of the unreacted dibromo-*o*-xylene.

Various attempts were made to determine the nature of the reactive *o*-xylylene species. In previous results,[14a] $\alpha,\alpha'$-dibromo-*m*-xylene reacted with metallic nickel to give a presumed *m*-xylene bis(nickel bromide) species **6**, which was effectively trapped with acetyl chloride to give the diketone product **7** in 62% yield (Scheme II). Attempted acetyl chloride trapping of an *o*-xylene bis(nickel bromide) species **8** in the reaction of metallic nickel with $\alpha,\alpha'$-dibromo-*o*-xylene failed to yield any diketone product **9**. These results suggest different mechanisms may be involved in the reactions of the *o*- and *m*-dibromoxylene isomers with metallic nickel.

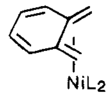
In conjuction with the above-mentioned trapping experiment, several attempts were made to isolate a nickel complex such as **10** analogous to the Pt complex **11**[17] or such as **12** similar to the Fe complex **13**[18] by using 1,5-cyclooctadiene, 2,2′-bipyridine, triethylphosphine, or triphenylphosphine as stabilizing ligands.



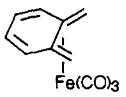
**10**



**11**



**12**



**13**

All attempts produced only *o*-xylylene polymer[19] and the ligand-coordinated nickel halide salts. Therefore, although the existence of an *o*-xylylene nickel complex in the reaction medium has not been disproven, such a complex if

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(15) Kerdesky, F. A. J.; Ardecky, R. J.; Lakshmikanthan, M. V.; Cava, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 1992.

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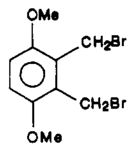
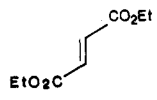
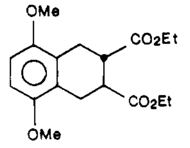
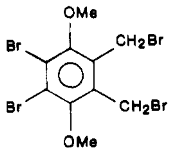
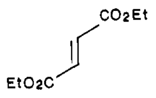
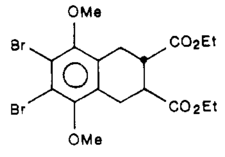
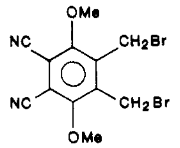
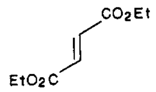
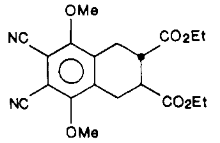
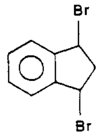
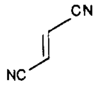
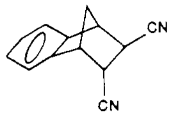
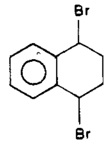
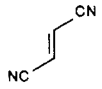
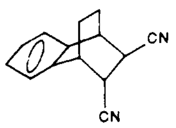
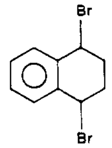
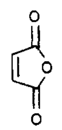
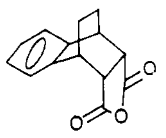
(17) Chappell, S. D.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 238.

(18) Roth, W. R.; Meier, J. D. *Tetrahedron Lett.* **1967**, 2053.

(19) Errede, L. A. *J. Polym. Sci.* **1961**, *49*, 253.

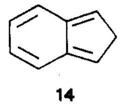
**Table II. Nickel-Mediated Cycloadditions of Substituted Dibromides with Dienophiles**[a]

| starting dihalides | dienophiles (molar equiv)[c] | adducts (% isolated yield)[b] |
|---|---|---|
|  |  (1.5) |  **34** (59) |
|  |  (1.5) |  **35** (41) |
|  |  (1.5) |  **36** (61) |
|  |  (2) |  **37** (66) |
|  |  (2) |  **38** (61) |
|  |  (2) |  **16** (46) |

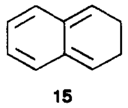
[a] All reactions were carried out at room temperature. [b] Isolated by silica gel chromatography. [c] Molar equivalents of dienophile are relative to starting dibromide.

present probably has limited stability which precludes its isolation at room temperature.

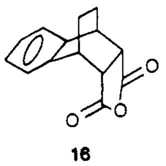
In addition to the *o*-xylylene intermediate **2**, isoindene (**14**) and 2,3-dihydronaphthalene (**15**) were generated by the 1,4-eliminations from 1,3-dibromoindan and 1,4-dibromotetralin, respectively, using activated nickel. The reactive intermediates **14** and **15** gave cycloadducts analogous to the reactions using **2** but with one or two carbon bridges, respectively. Both species reacted with fumaronitrile to give the bridged trans cycloadducts in moderate yields with no detectable amounts of either the cis-endo or cis-exo cycloadducts. The formation of exclusively the trans adducts is somewhat suprising in light of the results of cycloaddition using the parent *o*-xylylene intermediate **2** with fumaronitrile, which gave the mixture of cis and trans cycloadducts. The reaction of the 2,3-dihydronaphthalene species with maleic anhydride gave the known endo adduct **16**[20] in 46% yield with no detectable amount of the exo isomer. This result is similar in nature to the results reported by Warrener[21] in which generation of an isoindene intermediate and its trapping with *N*-methylmaleimide produced only the endo cycloadduct. This stereoselectivity is in good agreement with the "endo rule" for Diels–Alder reactions in which secondary orbital overlap directs formation of the endo adduct.



**14**

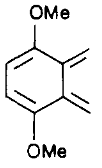


**15**

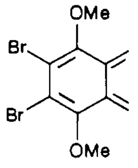


**16**

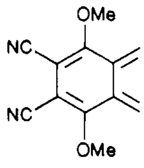
The substituted *o*-xylylene intermediates **18** and **19** demonstrate that electron-deficient substituents can be tolerated. The use of intermediates **17**, **18** and **19** provide a convenient entry into the synthesis of 1,4-naphthoquinones with electron-withdrawing groups in the 2,3,6,7-positions as well as just in the 6,7-positions.



**17**



**18**



**19**

In summary, the nickel-assisted generation of *o*-xylylene and substituted *o*-xylylenes represents a mild and convenient method for generation of this useful synthetic intermediate. While not all dienophiles are effective in trapping this intermediate, an extensive list has been shown to provide modest to good yields of the Diels–Alder products. Finally, it has been demonstrated that the *o*-xylylene intermediates can tolerate electron-withdrawing groups such as nitriles and halogens.

## Experimental Section

**General Data.** Melting points were determined on a Thomas Hoover melting point apparatus and are corrected. Boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer neat between NaCl plates or as KBr disks. $^1$H NMR spectra were recorded on a Varian EM-390 (90 MHz), Varian XL-200 (200 MHz), or Varian VXR-200 (200 MHz) spectrometer. Proton-decoupled $^{13}$C spectra were recorded at 50 MHz on a Varian VXR-200 or Varian XL-200 spectrometer. $^1$H and $^{13}$C chemical shifts are reported in ppm ($\delta$) using $Me_4Si$ as internal shift reference. High resolution mass spectra were performed by the Midwest Center for Mass Spectrometry at the University of Nebraska—Lincoln on a Kratos MS-80 mass spectrometer. Gas chromatography analysis was done on a Hewlett-Packard 5890A chromatograph using stainless steel columns packed with OV-17 (3%) on Chromosorb W or Chromosorb G.

All manipulations were carried out on a dual manifold vacuum/argon system. The Linde prepurified grade argon was further purified by passing it through a 150 °C catalyst column (BASF R3-11) and then through a column of phosphorous pentoxide followed by a column of granular potassium hydroxide. 1,2-Dimethoxyethane (DME) was freshly distilled under argon from sodium/potassium alloy. Anhydrous nickel iodide was purchased from Cerac, Inc. and was stored and charged into reaction vessels

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(20) (a) Schenck, G. O.; Kuhls, J.; Mannsfield, S.; Krauch, C. H. *Chem. Ber.* **1963**, *96*, 813. mp 196–197 °C. (b) Takeda, K.; Kitahonoki, K.; Sugiura, M.; Takano, Y. *Chem. Ber.* **1962**, *95*, 2344. mp 196.5–197.5 °C.

(21) Warrener, R. N.; Russell, R. A., Lee, T. S. *Tetrahedron Lett.* **1977**, *49*. Similar results were reported by Alder and Fremery[8a] using maleic anhydride as the dienophile.

under argon in a Vacuum Atmospheres Company drybox.[22] 1,4-Dibromo-1,2,3,4-tetrahydronaphthalene and 1,3-dibromoindan were prepared by the reaction of *N*-bromosuccinimide with 1,2,3,4-tetrahydronaphthalene and indan, respectively, in a manner similar to that reported by Djerassi.[23] 3,6-Dimethoxy-α,α′-dibromo-*o*-xylene,[24] 4,5-dibromo-3,6-dimethoxy-α,α′-dibromo-*o*-xylene,[25] and 4,5-dicyano-3,6-dimethoxy-α,α′-dibromo-*o*-xylene[26] were prepared according to literature methods. Other reagents were purchased from various commercial sources and were used as received.

**Typical Preparation of Activated Nickel.** A 50-mL three-necked flask was equipped with a rubber septum, addition funnel topped with rubber septum, condenser topped with argon inlet, and a Teflon-coated magnetic stir bar. The flask was charged with nickel iodide (5.595 g, 17.90 mmol), freshly cut lithium (0.2866 g, 41.30 mmol), and naphthalene (0.2302 g, 1.796 mmol) in the inert atmosphere drybox.[22] The flask was transferred to the manifold system and argon inlet fitted. Freshly distilled 1,2-dimethoxyethane (DME) was then added to the flask via syringe and the mixture stirred vigorously at room temperature. Within the first hour, the Li was pink colored within the reddish mixture. The reduction was complete within 12 h with all the Li consumed. The black Ni metal settled from a clear solution within 20–30 min. The clear solution above the slurry was removed via syringe and distilled DME (20 mL) added. The slurry was stirred for 1 min and Ni allowed to settle. This procedure was repeated twice to remove the naphthalene.

**Reaction of α,α′-Dibromo-*o*-xylene with Diethyl Fumarate in the Presence of Metallic Nickel.** To nickel powder prepared as described above from nickel iodide (5.595 g, 17.90 mmol) in a three-necked flask fitted with an addition funnel was added diethyl fumarate (4.930 g, 28.64 mmol) neat via syringe. α,α′-Dibromo-*o*-xylene (3.751 g, 14.21 mmol) dissolved in DME (20 mL) was then added slowly dropwise via an addition funnel over 1 h at room temperature with stirring to the nickel plus diethyl fumarate. The reaction mixture began to warm slightly and turn greenish within 5–10 min after beginning the addition of the α,α′-dibromo-*o*-xylene. Thin layer chromatography of reaction quenches showed the dibromide to be essentially consumed within 7 h. The greenish reaction mixture was allowed to stir a total of 24 h at room temperature and then was poured into 3% HCl (100 mL). The DME/HCl solution was then extracted with three portions (50 mL each) of dichloromethane. The dichloromethane extracts were washed with a solution of sodium bisulfite to remove residual iodine and then were dried over anhydrous sodium sulfate. Removal of the dichloromethane gave an oil which was chromatographed on silica gel (hexanes/hexanes:chloroform/chloroform) to give *trans*-2,3-dicarbethoxy-1,2,3,4-tetrahydronaphthalene (**24**)[9] (2.998 g, 76%) as an oil: bp 132–133 °C (0.23 mmHg); $^1$H NMR ($CDCl_3$, 200 MHz) 7.12 (m, 4 H), 4.20 (q, $J$ = 7.2 Hz, 4 H), 2.85–3.25 (m, 6 H), 1.29 (t, $J$ = 7.2 Hz, 6 H); $^{13}$C NMR ($CDCl_3$) 174.15, 133.84, 128.39, 126.15, 60.54, 42.11, 31.67, 14.02; IR (neat) 3020 (w), 2960 (m), 2920 (m), 1725 (s), 1370 (m), 1310 (m), 1255 (m), 1230 (m), 1215 (m), 1180 (s), 1145 (m), 1105 (m), 1025 (m), 745 (m) cm$^{-1}$.

**2-Carbomethoxy-1,2,3,4-tetrahydronaphthalene (20):**[5a,8b,9,10a] bp 76 °C (0.12 mmHg); $^1$H NMR ($CDCl_3$, 90 MHz), 1.57–2.35 (m, 2 H), 2.50–3.15 (m, 5 H), 3.70 (s, 3 H), 7.06 (m, 4 H); IR (neat) 3060 (w), 3020 (w), 2945 (m), 2840 (w), 1735 (s), 1490 (m), 1450 (m), 1430 (m), 1260 (m), 1220 (m), 1170 (s), 740 (s) cm$^{-1}$.

**2-Cyano-1,2,3,4-tetrahydronaphthalene (21):**[9,10a,11,13] bp 85 °C (0.11 mmHg); mp 54.5–55 °C; $^1$H NMR ($CDCl_3$, 90 MHz) 7.13 (m, 4 H), 3.27–2.65 (m, 5 H), 7.13 (m, 4 H); IR (KBr disk) 3020 (w), 2940 (w), 2840 (w), 2230 (w), 1490 (m), 1450 (m), 1430 (m), 750 (s) cm$^{-1}$.

**2,3-Dicarbomethoxy-1,4-dihydronaphthalene (28):**[11] $^1$H NMR ($CDCl_3$, 90 MHz) 3.70 (s, 4 H), 3.83 (s, 6 H), 7.17 (m, 4 H); IR (neat) 3000 (w), 2940 (w), 1720 (s), 1660 (m), 1430 (m), 1270 (s), 1225 (s), 1060 (m), 1025 (m), 750 (m) cm$^{-1}$.

**2-Carbomethoxy-2-(carbomethoxymethyl)-1,2,3,4-tetrahydronaphthalene (29):** bp 118 °C (0.16 mmHg); $^1$H NMR ($CDCl_3$, 90 MHz) 1.73–2.37 (m, 2 H), 2.43–3.45 (m, 6 H), 3.64 (s, 3 H), 3.69 (s, 3 H), 7.09 (m, 4 H); IR (neat) 3010 (w), 2940 (m), 2840 (w), 1735 (s, br), 1450 (m), 1430 (m), 1210 (s, br), 1165 (s, br), 740 (s) cm$^{-1}$.

***cis*- and *trans*-2,3-Dicarbomethoxy-1,2,3,4-tetrahydronaphthalene (2:1 Trans/Cis Mixture).** Cis isomer (**23**):[8b,9,11] $^1$H NMR (90 MHz, $CDCl_3$) 3.21 (br m, 6 H), 3.67 (s, 6 H), 7.13 (m, 4 H).

Trans isomer (**22**):[9,11] $^1$H NMR (90 MHz, $CDCl_3$) 3.03 (br m, 6 H), 3.71 (s, 6 H), 7.13 (m, 4 H).

***cis*- and *trans*-2,3-Dicarbethoxy-1,2,3,4-tetrahydronaphthalene (1:1 Trans/Cis Mixture).** Cis isomer (**25**):[9,13] $^1$H NMR (90 MHz, $CDCl_3$) 1.23 (t, 6 H), 3.16 (br m, 6 H), 4.13 (q, 4 H), 7.13 (m, 4 H).

Trans isomer (**24**):[9] $^1$H NMR (90 MHz, $CDCl_3$) 1.29 (t, 6 H), 3.03 (br m, 6 H), 4.18 (q, 4 H), 7.13 (m, 4 H). IR (neat, cis/trans mixture) 3020 (w), 2980 (m), 2930 (w), 1735 (s), 1725 (s), 1370 (m), 1180 (s, br), 1030 (br s), 740 (m) cm$^{-1}$.

***cis*- and *trans*-2,3-Dicyano-1,2,3,4-tetrahydronaphthalene (2:1 Trans/Cis Mixture).** Cis/Trans Mixture: $^1$H NMR (200 MHz, $CDCl_3$) 3.05–3.55 (m, 6 H), 7.05–7.35 (m, 4 H); $^{13}$C NMR ($CDCl_3$) trans (cis) 130.22 (130.11), 129.01 (129.14), 127.61 (127.58), 118.47 (117.98), 30.57 (30.50), 28.74 (28.69).

Trans isomer (**26**): mp 191.5–192.5 °C (recrystallized from $CHCl_3$/hexanes); $^1$H NMR (200 MHz, $CDCl_3$) 3.05–3.55 (m, 6 H), 7.05–7.35 (m, 4 H); $^{13}$C NMR ($CDCl_3$) 130.22, 129.01, 127.61, 118.48, 30.56, 28.73; IR (KBr disk) 3005 (w), 2920 (w), 2895 (w), 2240 (s), 1490 (s), 1435 (s), 1155 (w), 1110 (w), 905 (w), 765 (s) cm$^{-1}$.

***trans*-2-Carbomethoxy-3-methyl-1,2,3,4-tetrahydronaphthalene (30):** $^1$H NMR (200 MHz, $CDCl_3$) 1.06 (d, $J$ = 6.4 Hz, 3 H), 1.98–2.24 (m, 1 H), 2.36–2.60 (m, 2 H), 2.76–3.18 (m, 3 H), 3.73 (s, 3 H), 7.10 (m, 4 H); $^{13}$C NMR ($CDCl_3$) 175.94, 135.68, 134.63, 128.60, 128.49, 125.93, 125.84, 51.45, 47.63, 37.35, 32.60, 31.67, 19.85; IR (neat) 3020 (w), 2960 (m), 2930 (m), 1745 (s), 1500 (m), 1460 (m), 1440 (s), 1375 (m), 1325 (m), 1265 (m), 1240 (m), 1220 (m), 1195 (m), 1165 (s), 1028 (w), 1010 (w), 740 (s) cm$^{-1}$; mass spectrum, $m/e$ 204.1154, calcd for $C_{13}H_{16}O_2$ 204.1150; $m/e$ (relative intensity) 204 (26), 172 (17), 159 (11), 144 (100), 129 (97), 115 (26), 104 (20), 91 (24).

***cis*-1,2,3,4-Tetrahydronaphthalene-2,3-dicarboxylic acid anhydride (31):**[5a,8b,27] mp 184–185 °C; $^1$H NMR (90 MHz, $CDCl_3$) 2.73–3.32 (m, 4 H), 3.40–3.70 (m, 2 H), 7.21 (m, 4 H); IR (KBr disk) 2940 (w), 1850 (m), 1775 (s), 1233 (s), 1200 (s), 955 (s), 910 (s), 760 (s) cm$^{-1}$.

***cis*-1,2,3,4-Tetrahydronaphthalene-2,3-dicarboxylic acid (32):**[27] mp 193–194 °C (recrystallized from $CHCl_3$/acetone, dec to give anhydride **31**, mp 184–185 °C); $^1$H NMR (90 MHz, acetone-$d_6$) 2.93–3.50 (m, 6 H), 5.80 (br s, approx. 2 H), 7.10 (m, 4 H); IR (KBr disk) 3300–2400 (s, br), 1700 (s), 1690 (s), 1418 (m), 1318 (m), 1292 (m), 1260 (s), 1240 (m), 955 (m), 940 (m), 775 (m), 757 (m), 735 (m) cm$^{-1}$.

***cis*-2,3-Dibromoindan:**[8a,23] $^1$H NMR (200 MHz, $CDCl_3$) 2.94 (dt, 1 H, $J$ = 16.2, 2.8 Hz), 3.27 (dt, 1 H, $J$ = 16.2, 6.8 Hz), 5.50 (dd, 2 H, $J$ = 6.8, 2.8 Hz), 7.3–7.5 (m, 4 H); $^{13}$C NMR ($CDCl_3$) 142.69, 129.76, 125.71, 47.41, 47.16. (Note: The reaction of indan with *N*-bromosuccinimide was found in this case to surprisingly yield only the *cis*-dibromide isomer, as determined by the $^1$H and $^{13}$C NMR spectra of the product.)

**1,4-Dibromo-1,2,3,4-tetrahydronaphthalene:**[9,23] $^1$H NMR (200 MHz, $CDCl_3$) 2.20–2.50 (m, 2 H), 2.55–2.85 (m, 2 H), 5.60–5.68 (m, 2 H), 7.20–7.40 (m, 4 H); $^{13}$C NMR ($CDCl_3$) 135.75, 130.86, 129.02, 49.97, 28.83. (Note: As is the case with 2,3-dibromoindan mentioned previously, the reaction of 1,2,3,4-tetrahydronaphthalene with *N*-bromosuccinimide yields only one dibromide

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[22] In lieu of using a drybox, the $NiI_2$ can be weighed quickly in air and Li cut under mineral oil and rinsed with hexanes. Both are added to the flask which is then evacuated and refilled with argon several times. Reactions performed using Ni made by this procedure gave results indistinguishable from those in which the Li and $NiI_2$ were weighed in a drybox. The $NiI_2$ can be stored in a septum-capped flask for several months without noticeable effects on the nickel slurry reactivities.

[23] Djerassi, C. *Chem. Rev.* **1948**, *43*, 271.

[24] Horner, L.; Subramaniam, P. V.; Eiben, K. *Leibigs Ann. Chem.* **1968**, *714*, 91.

[25] Avram, M.; Dinulescu, I. G.; Dinu, D.; Mateescu, G.; Nenitzescu, C. *Tetrahedron* **1963**, *19*, 309.

[26] Newman, M. S.; Boden, H. *J. Org. Chem.* **1961**, *26*, 2525.

[27] Haworth, R. D.; Slinger, F. H. *J. Chem. Soc.* **1940**, 1321.

isomer, as determined by the $^1$H and $^{13}$C NMR spectra of the product. However, the exact stereochemisty of the product (cis or trans) has not been determined.)

***trans*-2,3-Dicyano-5,6-benzobicyclo[2.2.1]heptane (37)**:[28] $^1$H NMR (200 MHz, $CDCl_3$) 2.02–2.24 (qq, 2 H), 2.57–2.78 (dd, 1 H), 3.38–3.52 (dd, 1 H), 3.77–3.94 (m, 2 H), 7.20–7.50 (m, 4 H); $^{13}$C NMR ($CDCl_3$) 143.25, 141.29, 128.31, 128.22, 123.73, 121.71, 119.60, 118.23, 49.29, 47.94, 47.78, 36.57; IR (neat) 3080 (m), 3040 (w), 3000 (m), 2960 (m), 2890 (w), 2250 (s), 1475 (s), 1275 (m), 1193 (w), 1012 (w), 945 (m), 910 (s), 760 (s), 740 (s, br) cm$^{-1}$; mass spectrum, *m/e* 194.0840, calcd for $C_{13}H_{10}N_2$ 194.0844; *m/e* (relative intensity) 194 (11), 154 (7), 132 (7), 116 (100), 104 (6), 78 (74).

***trans*-2,3-Dicyano-5,6-benzobicyclo[2.2.2]octane (38)**:[28] $^1$H NMR (200 MHz, $CDCl_3$) 1.45–1.72 (m, 2 H), 1.85–2.09 (m, 1 H), 2.18–2.40 (m, 1 H), 2.73–2.90 (m, 1 H), 3.15–3.29 (m, 1 H), 3.35–3.52 (m, 2 H), 7.20–7.48 (m, 4 H); $^{13}$C NMR ($CDCl_3$) 138.97, 136.97, 128.29, 128.24, 125.73, 124.31, 119.32, 119.18, 37.28, 36.39, 34.05, 33.85, 24.62, 20.35; IR (neat) 3040 (m), 2960 (m), 2245 (m), 1490 (m), 1468 (m), 1455 (w), 1270 (w), 1220 (m), 755 (s, br) cm$^{-1}$; mass spectrum, *m/e* 208.1000, calcd for $C_{14}H_{12}N_2$ 208.1006; *m/e* (relative intensity) 208 (16), 153 (3), 140 (4), 130 (100), 115 (13), 91 (8), 84 (26), 78 (42).

***endo*-5,6-Benzobicyclo[2.2.2]octane-2,3-dicarboxylic acid anhydride (16)**:[19a,19b,28] mp 197–198 °C (recrystallized from hexanes/$CHCl_3$); $^1$H NMR (200 MHz, $CDCl_3$) 1.50–1.67 (m, 2 H), 1.78–1.95 (m, 2 H), 3.37 (app. t, 2 H), 3.62 (app. s, 2 H), 7.13–7.33 (m, 4 H); $^{13}$C NMR ($CDCl_3$) 172.00, 137.68, 128.05, 125.26, 45.31, 35.99, 23.91; IR (KBr disk) 3030 (w), 2960 (m), 2875 (m), 1863 (m), 1830 (w), 1780 (s, br), 1485 (m), 1460 (m), 1325 (m), 1305 (m), 1232 (m), 1215 (m), 1197 (m), 1083 (m, br), 938 (m), 900 (m), 775 (s), 743 (m) cm$^{-1}$; mass spectrum, *m/e* 228.0787, calcd for $C_{14}H_{12}O_3$ 228.0786; *m/e* (relative intensity) 228 (37), 200 (2), 156 (3), 141 (2), 130 (68), 129 (43), 128 (100), 115 (11), 100 (7).

***trans*-2,3-Dicarbethoxy-5,8-dimethoxy-1,2,3,4-tetrahydronaphthalene (34)**: mp 81–82 °C; $^1$H NMR (200 MHz, $CDCl_3$) 1.28 (t, 6 H), 2.90 (br m, 6 H), 3.77 (s, 6 H), 4.18 (q, 4 H), 6.63 (s, 2 H); $^{13}$C NMR ($CDCl_3$) 174.8, 151.1, 124.5, 107.5, 60.7, 55.7, 41.7, 26.6, 14.2; IR (KBr disk) 2930, 2820, 1715, 1590, 1462, 1430, 1293, 1245, 1175, 1075, 1010, 771 cm$^{-1}$; mass spectrum, *m/e* 336.1567, calcd for $C_{18}H_{24}O_6$ 336.1573. Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19; O, 28.54. Found: C, 64.13; H, 7.21; O, 28.47.

***trans*-6,7-Dibromo-2,3-dicarbethoxy-5,8-dimethoxy-1,2,3,4-tetrahydronaphthalene (35)**: mp >250 °C dec; $^1$H NMR (200 MHz, $CDCl_3$) 1.29 (t, 6 H), 3.00 (br m, 6 H), 3.78 (s, 6 H), 4.20 (q, 4 H); $^{13}$C NMR ($CDCl_3$) 173.6, 152.2, 129.4, 118.5, 60.8, 59.9, 41.1, 26.3, 14.0; IR (KBr disk) 2930, 1730, 1450, 1385, 1298, 1245, 1175, 1042, 940, 781 cm$^{-1}$; mass spectrum, *m/e* 490.9715 (M – H), calcd for $C_{18}H_{22}Br_2O_6$ 491.9783.

***trans*-2,3-Dicarbethoxy-6,7-dicyano-5,8-dimethoxy-1,2,3,4-tetrahydronaphthalene (36)**: mp 142 °C; $^1$H NMR (200 MHz, $CDCl_3$) 1.28 (t, 6 H), 3.00 (br m, 6 H), 4.06 (s, 6 H), 4.20 (q, 4 H); $^{13}$C NMR ($CDCl_3$) 173.1, 156.8, 136.4, 113.5, 105.1, 61.8, 61.4, 40.3, 25.7, 14.2; IR (KBr disk) 2990, 2950, 2220, 1730, 1458, 1405, 1305, 1246, 1191, 1047, 1020 cm$^{-1}$; mass spectrum, *m/e* 386.1473, calcd for $C_{20}H_{22}O_6N_2$ 386.1478. Anal. Calcd for $C_{28}H_{22}O_6N_2$: C, 62.17; H, 5.74; O, 24.84. Found: C, 61.86; H, 5.99; O, 25.25.

***α,α′*-Diiodo-*o*-xylene**:[29] mp 106–108 °C (lt. yellow); $^1$H NMR (200 MHz, $CDCl_3$) 4.56 (br s, 4 H), (4.59 imp., 4.62 imp.), 7.16–7.33 (m, 4 H); $^{13}$C NMR ($CDCl_3$) 1.77, (18.94 imp., 29.79 imp.), 128.92, (129.48 imp.), 130.73, (131.19 imp.), 137.34; IR (KBr disk) 1480 (w), 1440 (w, br), 1220 (m), 1195 (m), 1150 (s), 820 (w), 760 (s), 725 (m), 590 (w), 565 (s), 520 (s) cm$^{-1}$; mass spectrum, *m/e* 357.8712, calcd for $C_8H_8I_2$ 357.8713; *m/e* (relative intensity), 358 (1), (185 imp., 183 imp.), 127 (2), 104 (100), 78 (12).

**1,2-Bis(2-(iodomethyl)phenyl)ethane**:[19] mp 135–140 °C (white needles, rapidly decomposes); $^1$H NMR (200 MHz, $CDCl_3$) 3.08 (s, 4 H), 4.45 (s, 4 H), 7.13–7.40 (m, 8 H); IR (KBr disk) 3065 (w), 3025 (w), 2920 (w), 1600 (w), 1480 (m), 1453 (m), 1425 (m), 1150 (s), 788 (s), 763 (s), 697 (w), 575 (m), 522 (m), 480 (m) cm$^{-1}$; mass spectrum, (mol. ion $C_{16}H_{16}I_2$ not seen), *m/e* 335.0299 (M – I), calcd for $C_{16}H_{16}I$ 335.0296; *m/e* (relative intensity) 335 (17), 207 (100), 193 (55), 178 (27), 128 (19), 127 (10), 115 (26), 104 (73), 91 (14), 78 (22).

***o*-Xylylene polymer**:[10a,19] $^1$H NMR (90 MHz, $CDCl_3$) 2.80 (br s, 4 H), 7.07 (br s, 4 H); IR (neat) 3100–2910 (s, br), 1600 (w), 1490 (s), 1450 (s), 750 (s) cm$^{-1}$.

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(28) Although NMR data for these compounds were not found, tables of $^1$H NMR data for similar compounds have been reported. Tori, K.; Takano, Y.; Kitahonoki, K. *Chem. Ber.* **1963**, *97*, 2798.

(29) (a) Finkelstein, H. *Chem. Ber.* **1910**, *43*, 1532. (b) Parrini, V.; et al. *Gazz. Chim. Ital.* **1957**, *87*, 1147.