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# Rearrangements of the Diels−Alder Cycloadducts Obtained from Acetylenic Sulfones and 1,3-Diphenylisobenzofuran

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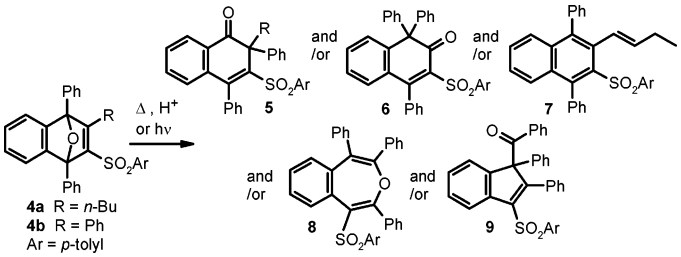
*Received March 18, 2006*




1,3-Diphenylisobenzofuran afforded Diels−Alder cycloadducts **4a**,**b** with *n*-butyl- and phenyl-substituted acetylenic sulfones **3a**,**b**, respectively. The products underwent various types of rearrangements under pyrolytic, acid-catalyzed, and photochemical conditions. In the presence of acid, or upon heating in xylenes, they afforded the ketones **5a**,**b**. In addition, the dehydration product **7a** was produced from the pyrolysis of **4a**, and the unexpected transposed ketone **6b** was generated under acid-catalyzed or pyrolytic conditions from **4b** via a postulated epoxide intermediate. The photolysis of **4a** afforded ketone **5a** as the sole isolated product, whereas **5b** afforded oxepin **8b** and indenyl phenyl ketone **9b**. The formation of the latter two products can be rationalized by a series of pericyclic reactions. These include an intramolecular [2+2] cycloaddition, followed by a 1,3-dipolar cycloreversion, for the transformation of **4b** to **8b** and a series of electrocyclic and [1,3]sigmatropic reactions to convert **8b** into **9b**.

1,3-Diphenylisobenzofuran (**1**) is a highly reactive diene that readily undergoes Diels−Alder cycloadditions with a wide range of dienophiles.[1−4] It has most notably served as a reagent for the preparation of various classes of polycyclic aromatic compounds, as well as for trapping unstable dienophiles. The aromatization of the benzene ring during cycloadditions provides a strong driving force for such processes.

Earlier studies have shown that a variety of further reactions of the Diels−Alder products obtained from **1** and various alkenes or acetylenes are possible under the conditions of the cycloadditions, upon subsequent workup, or upon treatment under acidic conditions. When an acetylene is employed as the dienophile, the resulting cycloadduct is an oxabenzonorbornadiene derivative **2** (Scheme 1), which lends itself readily to a variety of further transformations. These include hydrogenation and dehydration[5a] or deoxygenation[3,5c,6] to afford naphthalene derivatives, as well as spontaneous rearrangements to ketones,[7]or transformations that are promoted by acids,[5] silica gel,[8] or by the presence of a bridgehead alkylthio substituent.[9] The conversion of the initial cycloadducts derived from cyclopropenes and **1** to ketones or epoxides by oxygen via free radical reactions has also been reported.[10]

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(2) For reviews of the reactions, synthesis, and applications of benzofurans, including isobenzofurans, see: (a) Heaney, H.; Ahn, J. S. In *Comprehensive Heterocyclic Chemistry II*; Bird, C. W., Ed.; Elsevier: Oxford, 1996; Chapter 2.06, pp 297−350. (b) Friedrichsen, W. In *Comprehensive Heterocyclic Chemistry II*; Bird, C. W., Ed.; Elsevier: Oxford, 1996; Chapter 2.07, pp 351−393. (c) Keay, B. A.; Dibble, P. W. In *Comprehensive Heterocyclic Chemistry II*; Bird, C. W., Ed.; Elsevier: Oxford, 1996; Chapter 2.08, pp 395−436.

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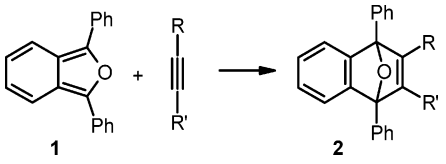
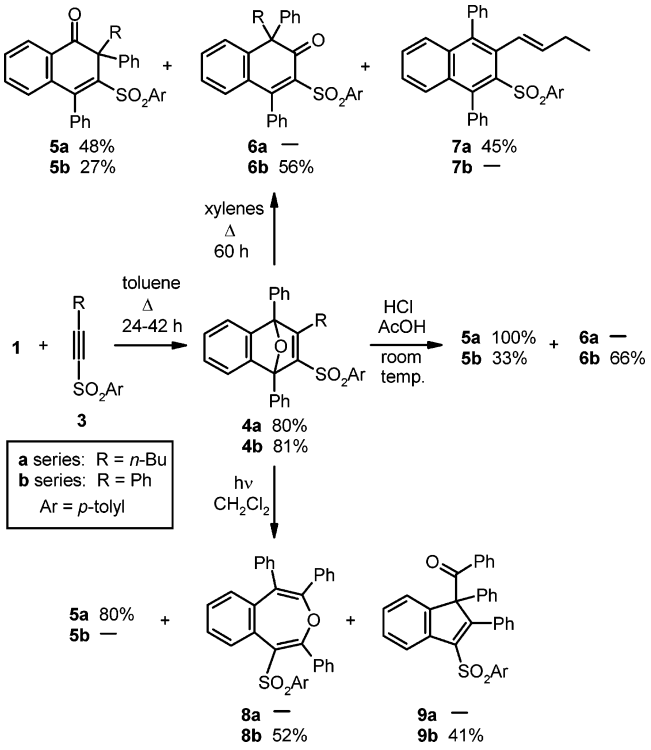
10.1021/jo060598e CCC: $33.50 
Published on Web 06/16/2006

**SCHEME 1**



**SCHEME 2**

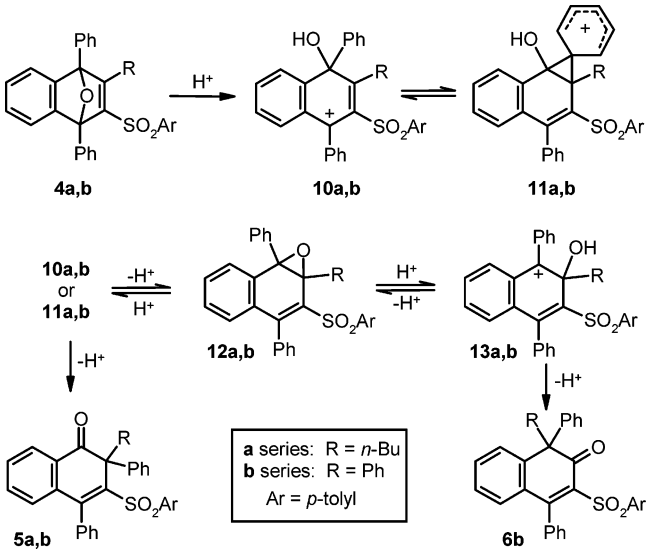



Among the acetylenic dienophiles that have been investigated to date, three fluorinated acetylenic sulfones underwent Diels−Alder reactions with **1**, affording the corresponding stable, isolable cycloadducts **2** [R = *n*-$C_4F_9SO_2$; R′ = Ph or *n*-Pr[11] and R = $CF_3SO_2$; R′ = 1-(8-iodonaphthyl)[6]]. Our ongoing interest in acetylenic sulfones[12,13] prompted us to investigate the cycloadditions of two representative nonfluorinated derivatives with **1**. We now report the results of these cycloadditions, along with a series of remarkable rearrangements of the resulting products.

## Results and Discussion

The cycloaddition of **1** with acetylenic sulfones **3a** and **3b** proceeded smoothly upon heating in toluene to afford the expected products **4a** and **4b** in high yield. The latter were then subjected to further transformations under pyrolytic, acid-catalyzed, and photolytic conditions. The results are summarized in Scheme 2. Thus, when heated for 60 h in xylenes at 150 °C, the butyl-substituted cycloadduct **4a** afforded the rearranged ketone **5a** and the alkenyl naphthalene **7a** in roughly equal amounts. The similar treatment of the cycloadduct **4b**, obtained from **1** and the phenyl-substituted acetylenic sulfone **3b**, produced **5b** (analogous to **5a**) along with the transposed ketone **6b** in the ratio of about 1:2. Under acid-catalyzed conditions, the reactions of **4a** and **4b** proceeded smoothly at room temperature. Thus, **5a** was the exclusive product from **4a**, while **4b** afforded a mixture of **5b** and **6b** similar to that obtained earlier under neutral conditions and elevated temperature. Finally, photolysis of the cycloadducts **4a** and **4b** in dichloromethane at 300 nm produced ketone **5a** as the only isolable product in the *n*-butyl series, while the corresponding analogue **5b** was completely absent in the phenyl series. Instead, **4b** afforded the benzoxepin **8b** and the indenyl phenyl ketone **9b** as the major and minor products. The structures of **4a**, **5a**, **5b**, **6b**, and **8b** were established unequivocally by X-ray crystallography, while those of **4b**, **7a**, and **9b** were deduced from spectroscopic data (see Experimental Section and Supporting Information).

**SCHEME 3**




A plausible mechanism for the rearrangement of **4a**,**b** to **5a**,**b** under acid-catalyzed conditions is shown in Scheme 3. The formation of carbocations **10a**,**b**, followed by a 1,2-shift of the phenyl substituent via the phenonium ions **11a**,**b**, would account for the formation of **5a**,**b**. This resembles the acid-catalyzed rearrangements of cycloadducts **2** [where R, R′ = $-(CH_2)_n-$], which were reported previously by Wittig and co-workers.[5c,d] The formation of **6b** from **4b** under similar conditions is more noteworthy, because it requires the formal 1,2-transposition of the bridging oxygen atom with that of the phenyl group. This can be rationalized by invoking an epoxide intermediate **12**, which can either regenerate **10** or produce the rearranged carbocation **13**. 1,2-Phenyl migration in **13b** leads to the observed isomeric ketone **6b**. Although the epoxides **12a**,**b** could not be isolated, their intermediacy in Scheme 3 is supported by the observation that **14a**, obtained by hydrogenation of **7a**, afforded the same rearranged ketone **5a** when treated with MCPBA, under conditions which are expected to produce the same epoxide **12a** (Scheme 4).[14] The formation of the transposed

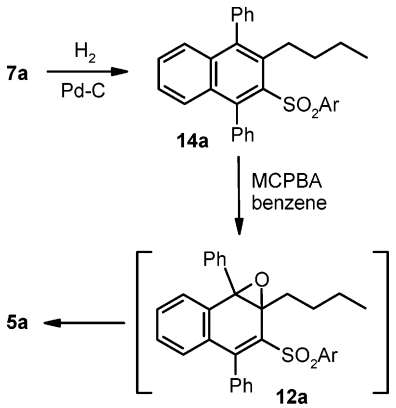
(11) (a) Hanack, M.; Massa, F. *Tetrahedron Lett.* **1977**, 661. (b) Massa, F.; Hanack, M.; Subramanian, L. R. *J. Fluorine Chem.* **1982**, *19*, 601.

(12) For a review of acetylenic and allenic sulfones, see: Back, T. G. *Tetrahedron* **2001**, *57*, 5263.

(13) For recent examples, see: (a) Back, T. G.; Hamilton, M. D.; Lim, V. J. J.; Parvez, M. *J. Org. Chem.* **2005**, *70*, 967. (b) Back, T. G.; Parvez, M.; Wulff, J. E. *J. Org. Chem.* **2003**, *68*, 2223. (c) Back, T. G.; Nakajima, K. *J. Org. Chem.* **2000**, *65*, 4543. (d) Back, T. G.; Nakajima, K. *J. Org. Chem.* **1998**, *63*, 6566.

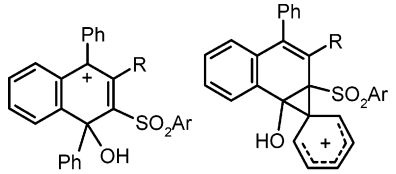
(14) For the oxidation of other polycyclic arenes with peracids, see: Lewis, S. N. In *Oxidation*; Augustine, R. L., Ed.; Dekker: New York, 1969; Vol. 1, pp 235−236.

**SCHEME 4**



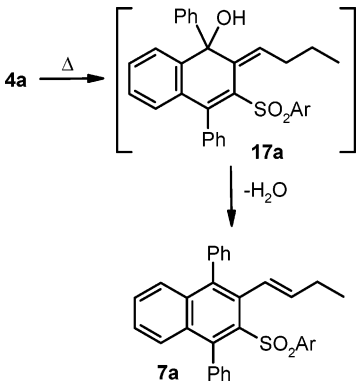

ketone **6b** in the phenyl series, but not of **5b** in the butyl series, can be attributed to the generally more facile migration of the phenyl group in cation **13b** compared to that of an *n*-butyl group in cation **13a**.[15]

The absence of any noticeable amounts of the regioisomeric products of **5a**,**b** and **6b**, which would result from the acid-catalyzed cleavage of the other C−O bond in **4a**,**b**, is noteworthy. This is attributed to the greater expected stability resulting from the cross-conjugation of the delocalized cation with the sulfone moiety in **10a**,**b**, compared to the linear conjugation in the regioisomeric species **15a**,**b**, because the electron-withdrawing sulfone group is expected to destabilize the respective cations. Similarly, **16a**,**b** is expected to be destabilized relative to **11a**,**b** by the proximity of the sulfone moiety.[16]

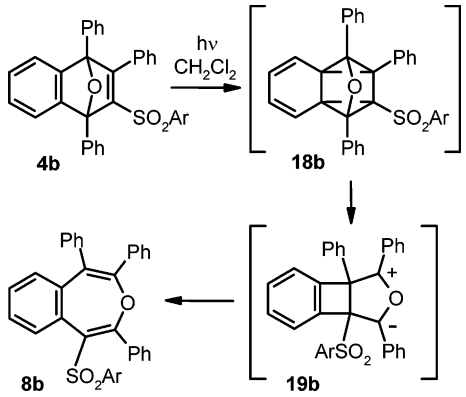



The reactions in Scheme 2 that were performed under neutral pyrolytic conditions resemble the acid-catalyzed process in the case of the phenyl series, affording comparable amounts of the principal products **5b** and **6b** from **4b**. On the other hand, **4a** in the butyl series produced a new product **7a**, along with a comparable amount of the previously observed **5a**. The formation of **7a** can be rationalized by the elimination and ring-opening of the oxygen bridge in **4a** to generate **17a**, followed by elimination of water and aromatization (Scheme 5). Inclusion

**SCHEME 5**




**SCHEME 6**




of either 0.2 or 2.0 mol of the radical inhibitor 2,6-di-*tert*-butyl-4-cresol (butylated hydroxytoluene, BHT) did not suppress the formation of the above products. This suggests that **4a** and **4b** undergo heterolytic C−O bond cleavage to produce dipolar, rather than diradical, intermediates in the pyrolytic reaction.

The photolysis of the butyl derivative **4a** afforded the same ketone **5a** that had been previously observed as the sole or major product under acid-catalyzed or pyrolytic conditions, respectively. In contrast to the pyrolytic conversion of **4a** to **5a**, the photochemical formation of **5a** was suppressed by the inclusion of BHT, suggesting that, under these conditions, the photochemical process does proceed via a radical pathway. However, in the phenyl series, **4b** produced no significant amounts of either ketone **5b** or **6b**. Instead, the benzoxepin **8b** and exocyclic ketone **9b** were obtained. Earlier photochemical experiments on 7-oxanorbornadienes revealed that such systems undergo formal intramolecular photochemical [2+2] cycloadditions to the corresponding oxaquadricyclanes, followed by thermal isomerization to oxepins via carbonyl ylides.[17] A similar process is shown in Scheme 6, where the photoisomerization of **4b** via oxaquadricyclane **18b** and ylide **19b** affords the observed product **8b**.

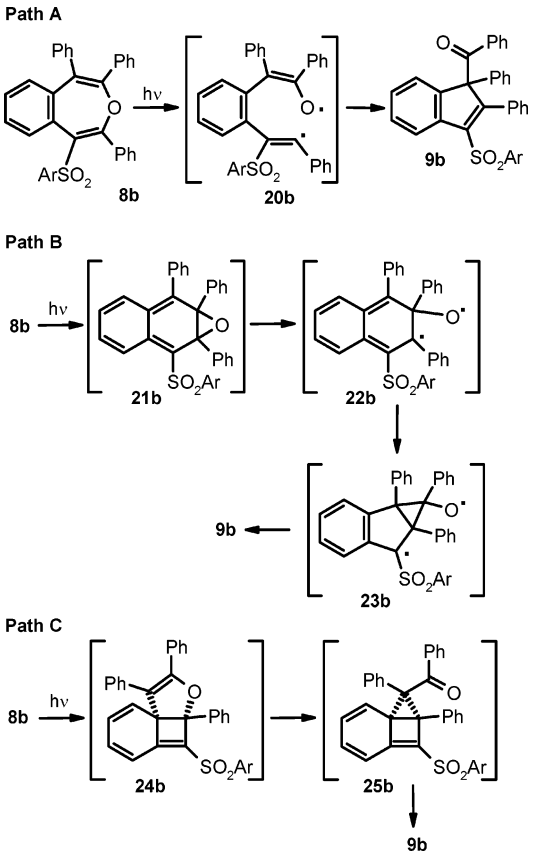
Moreover, control experiments revealed that photolysis of pure benzoxepin **8b** under similar conditions resulted in its conversion to ketone **9b**, whereas this transformation failed in the dark. This indicates that **9b** is produced from the further

(15) For lead references and a discussion of the migratory aptitudes of various types of substituents, see: Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 5th ed.; Wiley: New York, 2001; pp 1384−1386.

(16) On the other hand, preliminary molecular modeling performed by subjecting **10a**,**b**, **11a**,**b**, **15a**,**b**, and **16a**,**b** to MMFF conformation searches and PM3 geometry optimizations, followed by 3-21G* ab initio single-point energy calculations (Spartan 2004 for Windows platform; Wave function, Inc.), suggests that **15a**,**b** and **16a**,**b** are stabilized relative to **10a**,**b** and **11a**,**b**, respectively, by intramolecular hydrogen bonding between their hydroxyl groups and one of their sulfone oxygen atoms. Higher level computations will be required to establish more precisely the relative roles of resonance, inductive, and hydrogen-bonding effects in determining the regioselectivity of these processes.

(17) (a) Prinzbach, H.; Arguëlles, M.; Druckrey, E. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 1039. (b) Vogel, P.; Willhalm, B.; Prinzbach, H. *Helv. Chim. Acta* **1969**, *52*, 584. (c) Tochtermann, W.; Olsson, G. *Chem. Rev.* **1989**, *89*, 1203. (d) Tochtermann, W.; Timm, H.; Diekmann, J. *Tetrahedron Lett.* **1977**, 4311. (e) Tochtermann, W.; Köhn, H. *Chem. Ber.* **1980**, *113*, 3249.

**SCHEME 7**

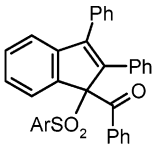



photoisomerization of the benzoxepin **8b** rather than via an independent pathway from **4b** or via a thermal process from **8b**.

Several possible pathways for the transformation of **8b** to **9b** have at least partial precedent in the literature and are summarized in Scheme 7. A diradical mechanism was suggested as a possible pathway for the related photoisomerization of 4,5-dihydrooxepin to 2-cyclopentenecarbaldehyde via homolytic cleavage of a C−O bond, followed by radical recombination.[18] This corresponds to path A in Scheme 7. Alternatively, the photochemical interconversions of arene oxides with the corresponding oxepins have been extensively studied in polycyclic aromatic hydrocarbon systems.[19] Electrocyclic ring closures have been proposed for these transformations.[19a,d,e] The analogous process here would lead to epoxide **21b** from **8b**, which could then undergo further rearrangement to **9b**, possibly via diradicals **22b** and **23b** (path B in Scheme 7) or similarly by means of dipolar intermediates. A third possibility is based on earlier work by Tochtermann et al.[20] who reported that the photolysis of certain 3,6-alkanooxepins produced the corresponding cyclopentadienecarbaldehydes via a series of fused-ring dihydrofurans and cyclopropanecarbaldehydes. Evidence for this pathway was based on NMR detection of the intermediates. Formally, one can envisage these transformations taking place by means of a 4$\pi$-electron electrocyclic ring closure, followed by a [1,3]sigmatropic rearrangement and a 4$\pi$-electron electrocyclic cycloreversion to the cyclopentadienecarbaldehyde. A similar mechanism in the present case would proceed via intermediates **24b** and **25b** and is shown in path C of Scheme 7.

We repeated the photoisomerization of **8b** to **9b** in the presence of the radical inhibitor BHT but observed no significant change in the rate or nature of the products of the reaction. While this experiment does not unequivocally rule out the possibility of radical intermediates, it is most consistent with path C, where radical intermediates are not required. Furthermore, the photochemical 6$\pi$-electron electrocyclic reaction required to convert **8b** to epoxide **21b** in path B would require a conrotatory ring closure that would lead to a highly strained *trans*-epoxide. Path B, therefore, appears unlikely if one assumes a concerted mechanism for the formation of **21b**. On the other hand, a photochemical 4$\pi$-electron electrocyclic ring closure of **8b** to **24b** in path C would be disrotatory and would, therefore, lead to the less-strained *cis*-fused dihydrofuran−cyclobutene system. The subsequent sigmatropic rearrangement of **24b** to **25b** would be expected to proceed with retention of configuration under photochemical conditions to again afford a *cis*-fused cyclopropane moiety. Based on the above considerations and on precedents with analogous systems, we tentatively favor the Tochtermann mechanism shown in path C for the formation of **9b** from **8b**.[21]

The conversion of **8b** to **9b** was also highly regioselective, and the isomer **26b** was not observed. The reason for the difference in behavior of **4a** and **4b** under photochemical conditions is unclear at this time and requires further investigation.




**26b** (Ar = *p*-tolyl)

In conclusion, the cycloaddition of 1,3-diphenylisobenzofuran (**1**) with acetylenic sulfones **3a** and **3b** afforded the expected Diels−Alder cycloadducts **4a** and **4b**. The further transformations of the latter products under acid-catalyzed and pyrolytic conditions resulted in the regioselective formation of rearranged ketones **5a** and **5b**, as well as the dehydration product **7a**, from the pyrolysis of **4a**. The remarkable formation of ketone **6b** from **4b** was rationalized by invoking an epoxide intermediate that provides a pathway for the transposition of the oxygen functionality. Although **4a** again produced ketone **5a** under photochemical conditions, different products were observed from **4b**. Thus, benzoxepin **8b** was the initial product via a postulated intramolecular [2+2] cycloaddition leading to an oxaquadricyclane intermediate, followed by isomerization via a carbonyl

(18) Cockroft, R. D.; Waali, E. E.; Rhoads, S. J. *Tetrahedron Lett.* **1970**, 3539.

(19) For example, see: (a) Balani, S. K.; Brannigan, I. N.; Boyd, D. R.; Sharma, N. D.; Hempenstall, F.; Smith, A. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1091. (b) Agarwal, R.; Boyd, D. R. *J. Chem.* Soc., Perkin Trans. 1 **1993**, 2869. (c) Boyd, D. R.; Sharma, N. D.; Agarwal, S. K.; Gadaginamath, G. S.; O'Kane, G. A.; Jennings, W. B.; Yagi, H.; Jerina, D. M. *J. Chem. Soc., Perkin Trans. 1* **1993**, 423. (d) Boyd, D. R.; Agarwal, S. K.; Balani, S. K.; Dunlop, R.; Gadaginamath, G. S.; O'Kane, G. A.; Sharma, N. D.; Jennings, W. B.; Yagi, H.; Jerina, D. M. *J. Chem. Soc., Chem. Commun.* **1987**, 1633. (e) Shudo, K.; Okamoto, T. *Chem. Pharm. Bull.* **1973**, *21*, 2809. (f) Griffin, G. W.; Satra, S. K.; Brightwell, N. E.; Ishikawa, K.; Bhacca, N. S. *Tetrahedron Lett.* **1976**, 1239.

(20) (a) Heber, D.; Rösner, P.; Tochtermann, W. *Eur. J. Org. Chem.* **2005**, 4231. (b) Sczostak, A.; Sönnichsen, F.; Tochtermann, W.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Tetrahedron Lett.* **1985**, *26*, 5677. (c) Tochtermann, W.; Olsson, G.; Sczostak, A.; Sönnichsen, F.; Frauenrath, H.; Runsink, J.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1989**, *122*, 199.

ylide. The exocyclic ketone **9b** was produced by further irradiation of **8b**, rather than via an independent pathway from **4b**. The transformation of **8b** to **9b** is consistent with a mechanism involving successive pericyclic reactions: an electrocyclic ring closure, a [1,3]sigmatropic rearrangement, and an electrocyclic ring opening. These processes further illustrate the rich and diverse behavior of **1** and its Diels−Alder cycloadducts.

## Experimental Section

Acetylenic sulfones **3a**[13c] and **3b**[22] were prepared as descrbed previously.

**Cycloaddition of 1,3-Diphenylisobenzofuran (1) with 1-(*p*-Toluenesulfonyl)-1-hexyne (3a).** A solution of **1** (567 mg, 2.10 mmol) and **3a** (472 mg, 2.00 mmol) in toluene (4.5 mL) was heated in a sealed V-vial at 109 °C for 1 d. The mixture was concentrated under reduced pressure and separated by flash chromatography (elution with 10% ethyl acetate−hexanes) to afford 806 mg (80%) of the cycloadduct **4a** as a light yellow oil. Crystallization from ethyl acetate−hexanes gave white crystals: mp 159−164 °C; IR (KBr) 1600, 1452, 1317, 1146 cm$^{-1}$; $^1$H NMR (300 MHz) $\delta$ 7.88−7.78 (m, 4H), 7.63−7.44 (m, 5H), 7.36−7.29 (m, 3H), 7.15−7.06 (m, 4H), 6.99 (d, $J$ = 8.2 Hz, 2H), 2.94 (ddd, $J$ = 12.3, 10.5, 5.3 Hz, 1H), 2.66 (ddd, $J$ = 12.0, 10.5, 4.3 Hz, 1H), 2.34 (s, 3H), 1.36−0.98 (m, 4H), 0.80 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz) $\delta$ 171.8, 149.7, 148.2, 147.9, 143.4, 137.9, 134.0, 133.5, 129.0, 128.6, 128.5, 128.3, 128.1, 127.7, 127.2, 126.6, 125.9, 125.4, 121.4, 120.9, 93.4, 91.6, 30.1, 26.5, 22.7, 21.5, 13.6; MS (*m*/*z*, %) 506 (M$^+$, 0.4), 350 (100), 270 (99), 105 (98), 77 (73); HRMS calcd for $C_{33}H_{30}O_3S$ (M$^+$), 506.1916; found, 506.1961. Anal. Calcd for $C_{33}H_{30}O_3S$: C, 78.23; H, 5.97. Found: C, 77.89; H, 5.76. The structure was confirmed by X-ray crystallography (see Supporting Information).

Further elution with 15% ethyl acetate−hexanes gave 49 mg (5%) of **5a** as a light yellow oil (vide infra).

**Cycloaddition of 1,3-Diphenylisobenzofuran (1) with 1-Phenyl-2-(*p*-toluenesulfonyl)ethyne (3b).** A solution of **1** (567 mg, 2.10 mmol) and **3b** (512 mg, 2.00 mmol) in toluene (4.5 mL) was heated in a sealed V-vial at 124 °C for 42 h. The reaction mixture was concentrated under reduced pressure and separated by flash chromatography (elution with 40% pentane−dichloromethane) to afford 852 mg (81%) of **4b** as a light yellow oil. Crystallization from methanol gave white crystals: mp 200−202 °C; IR (KBr) 1595, 1450, 1312, 1304, 1143 cm$^{-1}$; $^1$H NMR (300 MHz) $\delta$ 8.05 (d, $J$ = 6.7 Hz, 2H), 7.81 (d, $J$ = 6.7 Hz, 1H), 7.57−7.37 (m, 5H), 7.34−7.21 (m, 6H), 7.16 (d, $J$ = 7.2 Hz, 1H), 7.09 (d, $J$ = 8.2 Hz, 1H), 7.07 (d, $J$ = 7.2 Hz, 1H), 6.89 (d, $J$ = 7.2 Hz, 2H), 6.71−6.62 (m, 4H), 2.17 (s, 3H); $^{13}$C NMR (75 MHz) $\delta$ 167.1, 153.4, 149.9, 149.6, 143.2, 136.9, 133.9, 132.5, 132.2, 129.33, 129.32, 129.2, 128.9, 128.8, 128.39, 128.37, 128.2, 127.7, 127.3, 126.1, 125.7, 123.3, 122.3, 95.7, 95.4, 21.5; MS (*m*/*z*, %) 526 (M$^+$, 0.2), 510 (0.7), 371 (100), 270 (78); HRMS calcd for $C_{35}H_{26}O_3S$ (M$^+$), 526.1603; found, 526.1628. Anal. Calcd for $C_{35}H_{26}O_3S$: C, 79.82; H, 4.98. Found: C, 79.60; H, 4.98.

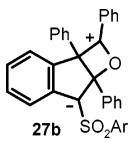
**Pyrolysis of Cycloadduct 4a.** A solution of **4a** (342 mg, 0.676 mmol) in xylenes (4 mL) was heated in a sealed V-vial at 150 °C for 60 h. The mixture was concentrated under reduced pressure to afford a colorless oil that was separated by flash chromatography (elution with 50% pentane−dichloromethane) to afford 149 mg (45%) of 2-(*trans*-1-butenyl)-1,4-diphenyl-3-(*p*-toluenesulfonyl)-naphthalene (**7a**) as a colorless oil: IR (film) 1595, 1440, 1321, 1150 cm$^{-1}$; $^1$H NMR (300 MHz) $\delta$ 7.54−7.30 (m, 14H), 7.22−7.14 (m, 2H), 7.12 (d, $J$ = 8.2 Hz, 2H), 6.42 (dt, $J$ = 16.1, 1.5 Hz, 1H), 4.93 (dt, $J$ = 16.1, 6.7 Hz, 1H), 2.36 (s, 3H), 1.80−1.68 (m, 2H), 0.56 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz) $\delta$ 142.8, 142.0, 141.1, 140.7, 139.9, 139.3, 137.7, 135.9, 134.34, 134.30, 132.5, 130.9, 130.3, 128.8, 128.31, 128.26, 128.0, 127.5, 127.4, 127.2, 126.92, 126.88, 126.34, 126.26, 26.2, 21.5, 12.6; MS (*m*/*z*, %) 488 (M$^+$, 94), 381 (81), 302 (97), 119 (71), 105 (100); HRMS calcd for $C_{33}H_{28}O_2S$ (M$^+$), 488.1810; found, 488.1820.

Further elution (50% pentane−dichloromethane) provided 164 mg (48%) of 2-*n*-butyl-2,4-diphenyl-3-(*p*-toluenesulfonyl)-2*H*-naphthalen-1-one (**5a**) as a light yellow oil. Crystallization from ethyl acetate−hexanes gave white crystals: mp 186−188 °C; IR (KBr) 1677, 1594, 1447, 1315, 1301, 1137 cm$^{-1}$; $^1$H NMR (300 MHz) $\delta$ 8.17−8.11 (m, 1H), 7.51−7.29 (m, 10H), 6.97 (td, $J$ = 7.2 Hz, 1.6 Hz, 1H), 6.84 (d, $J$ = 8.2 Hz, 2H), 6.71−6.66 (m, 1H), 6.61 (d, $J$ = 8.2 Hz, 2H), 6.52 (d, $J$ = 7.7 Hz, 1H), 3.37 (td, $J$ = 12.8 Hz, 4.1 Hz, 1H), 3.01 (td, $J$ = 12.8 Hz, 4.1 Hz, 1H), 2.30 (s, 3H), 1.92−1.75 (m, 1H), 1.58−1.42 (m, 2H), 1.19−1.04 (m, 1H), 0.96 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz) $\delta$ 198.4, 148.1, 144.2, 142.7, 141.1, 139.6, 137.9, 134.7, 134.1, 131.9, 130.6, 130.2, 129.2, 128.7, 128.6, 128.3, 128.1, 127.9, 127.8, 127.5, 127.4, 127.2, 126.8, 60.2, 36.3, 26.9, 23.2, 21.4, 13.9; MS (*m*/*z*, %) 506 (M$^+$, 0.2), 449 (13), 351 (100), 307 (30), 295 (56), 265 (41), 219 (65), 91 (59); HRMS calcd for $C_{33}H_{30}O_3S$ (M$^+$), 506.1916; found, 506.1937. Anal. Calcd for $C_{33}H_{30}O_3S$: C, 78.23; H, 5.97. Found: C, 77.92; H, 5.96. The structure was confirmed by X-ray crystallography (see Supporting Information).

**Pyrolysis of Cycloadduct 4b.** A solution of **4b** (150 mg, 0.285 mmol) in xylenes (4 mL) was heated in a sealed V-vial at 155 °C for 60 h. The solution was cooled to room temperature, and the reaction mixture was concentrated under reduced pressure. The residue was triturated with hot methanol and filtered. The white solid was washed with methanol and dried to afford 41 mg (27%) of 2,2,4-triphenyl-3-(*p*-toluenesulfonyl)-2*H*-naphthalen-1-one (**5b**), obtained as white crystals: mp 294.5−295.5 °C (from dichloromethane−methanol); IR (KBr) 1680, 1590, 1449, 1323, 1151 cm$^{-1}$; $^1$H NMR (300 MHz) $\delta$ 8.03−7.98 (m, 1H), 7.80−7.73 (m, 4H), 7.47−7.29 (m, 11H), 7.12 (d, $J$ = 7.2 Hz, 2H), 6.73 (d, $J$ = 8.2 Hz, 2H), 6.71−6.65 (m, 1H), 6.00 (d, $J$ = 8.7 Hz, 2H), 2.26 (s, 3H); $^{13}$C NMR (75 MHz) $\delta$ 198.2, 147.9, 145.5, 143.0, 139.2, 139.1, 137.9, 134.7, 134.5, 131.1, 130.8, 130.7, 129.2, 128.3, 128.12, 128.07, 128.03, 127.98, 127.8, 127.7, 66.8, 21.4; MS (*m*/*z*, %) 371 (M$^+$ − Ts, 100), 309 (12), 293 (13), 265 (15). Anal. Calcd for $C_{35}H_{26}O_3S$: C, 79.82; H, 4.98. Found: C, 80.13; H, 4.96. The structure was confirmed by X-ray crystallography (see Supporting Information).

The methanol filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel (elution with 20% pentane−dichloromethane) to afford 84 mg (56%) of 1,1,4-triphenyl-3-(*p*-toluenesulfonyl)-1*H*-naphthalen-2-one (**6b**), obtained as yellow crystals: mp 187−193 °C (from methanol); IR (KBr) 1700, 1684, 1443, 1321, 1148 cm$^{-1}$; $^1$H NMR (300 MHz) $\delta$ 7.47−7.40 (m, 3H), 7.39−7.16 (m, 12H), 7.04 (d, $J$ = 8.2 Hz, 2H), 6.95 (dd, $J$ = 8.2, 1.5 Hz, 1H), 6.82−6.76 (m, 4H), 6.73 (dd, $J$ = 7.7, 1.5 Hz, 1H), 2.39 (s, 3H); $^{13}$C NMR (75 MHz) $\delta$ 195.0, 156.3, 144.2, 143.4, 139.2, 137.5, 134.8, 134.3, 132.2, 131.5, 131.4, 131.2,

(21) We thank a reviewer for suggesting an alternative pathway for the conversion of **8b** to **9b** via the zwitterionic intermediate **27b**, a possibility that we cannot rule out at this time. Zwitterionic intermediates have been proposed in the somewhat related photochemical rearrangements of cyclohexadienones and bicyclo[3.1.0]hex-3-en-2-ones (skeletal isomers of oxepins), but this has not been without controversy. For some key references, see: (a) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1961**, *83*, 4486. (b) Schultz, A. G.; Reilly, J. *J. Am. Chem. Soc.***1992**, *114*, 5068. (c) Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.* **1980**, *45*, 4864. (d) Schuster, D. I. *Acc. Chem. Res.* **1978**, *11*, 65. For a different point of view, see: (e) Gómez, I.; Olivella, S.; Reguero, M.; Riera, A.; Solé, A. *J. Am. Chem. Soc.* **2002**, *124*, 15375.



**27b**

(22) Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1983**, *48*, 3077.

130.2, 129.0, 128.8, 128.7, 128.2, 128.1, 127.9, 127.72, 127.68, 69.6, 21.5; MS (*m*/*z*, %) 526 ($M^+$, 0.5), 371 (58), 330 (100), 265 (40); HRMS calcd for $C_{35}H_{26}O_3S$ ($M^+$), 526.1603; found, 526.1635. Anal. Calcd for $C_{35}H_{26}O_3S$: C, 79.82; H, 4.98. Found: C, 79.68; H, 5.25. The structure was confirmed by X-ray crystallography (see Supporting Information).

**Acid-Catalyzed Rearrangement of Cycloadduct 4a.** A solution of **4a** (16 mg, 0.032 mmol) in 5 mL of acetic acid and 0.5 mL of concentrated HCl was stirred at room temperature for 1 d to afford 16 mg (quantitative) of **5a** as a homogeneous colorless oil with properties identical to those of **5a** obtained via pyrolysis of **4a** (vide infra).

**Acid-Catalyzed Rearrangement of Cycloadduct 4b.** A solution of **4b** (10 mg, 0.019 mmol) in acetic acid (5 mL) and 0.5 mL of concentrated HCl was stirred at room temperature for 4 d to afford 10 mg (quantitative) of a yellow oil that consisted of ketones **5b** and **6b** (vide infra) in the ratio of 2:1 (NMR analysis).

**Hydrogenation and MCPBA Oxidation of 7a.** Product **7a** (89 mg, 0.18 mmol) was dissolved in 8 mL of methanol, and palladium hydroxide on carbon (64 mg) was added. The mixture was hydrogenated at 1 atm for 4 d. After filtration of the mixture through a pad of Celite, the methanol was evaporated, and the residue was separated by flash chromatography (elution with 40% pentane−dichloromethane) to afford 78 mg (88%) of **14a** as a colorless oil: IR (film) 1598, 1439, 1316, 1151 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ 7.57−7.42 (m, 3H), 7.40−7.17 (m, 11H), 7.17−7.07 (m, 4H), 3.09−2.98 (m, 2H), 2.38 (s, 3H), 1.50−1.38 (m, 2H), 1.08 (sextet, $J$ = 7.2 Hz, 2H), 0.65 (t, $J$ = 7.2 Hz, 3H); $^{13}C$ NMR (75 MHz) $\delta$ 142.7, 142.6, 141.7, 139.0, 137.6, 137.1, 136.2, 134.7, 132.1, 130.9, 130.3, 129.2, 128.4, 128.2, 128.0, 127.5, 127.2, 127.1, 126.5, 126.2, 125.9, 34.1, 31.6, 23.1, 21.5, 13.4; MS (*m*/*z*, %) 490 ($M^+$, 53), 455 (100), 291 (53); HRMS calcd for $C_{33}H_{30}O_2S$ ($M^+$), 490.1967; found, 490.1989.

A solution of **14a** (38 mg, 0.077 mmol) and MCPBA (77%, 1.0 mmol) in benzene (3 mL) was sealed in a V-vial and heated at 90 °C for 62 h. After the solution was cooled to room temperature, the reaction mixture was washed with 10% aqueous $KHCO_3$ solution, and the aqueous layer was extracted with dichloromethane. The organic layer was dried and evaporated, and the residue was purified by flash chromatography (elution with 40% pentane−dichloromethane) to afford 19 mg (50%) of the starting material and 13 mg (34%) of ketone **5a**, identical to the sample prepared from **4a**.

**Photolysis of Cycloadduct 4a.** A solution of **4a** (30 mg, 0.057 mmol) in 4 mL of dichloromethane was irradiated for 2 d in a Rayonet reactor equipped with 300 nm lamps. The solvent was evaporated, and the residue was purified by flash chromatography (15% ethyl acetate−hexanes) to afford 24 mg (80%) of ketone **5a**.

**Photolysis of Cycloadduct 4b.** A solution of **4b** (203 mg, 0.386 mmol) in 4 mL of dichloromethane was irradiated for 2 d, as in the preceding experiment. The solvent was evaporated, and the residue was purified by flash chromatography (14% ethyl acetate−hexanes) to afford 103 mg (51%) of 2,3,7-triphenyl-6-(*p*-toluenesulfonyl)-4,5-benzoxepin (**8b**), obtained as white crystals: mp 225−227 °C (from hexanes/ethyl acetate); IR (KBr) 1595, 1442, 1318, 1148 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ 8.27 (d, $J$ = 8.1 Hz, 1H), 7.47 (d, $J$ = 8.7 Hz, 2H), 7.42−7.08 (m, 17H), 6.75 (d, $J$ = 8.2 Hz, 1H), 6.56 (d, $J$ = 7.2 Hz, 2H), 2.39 (s, 3H); $^{13}C$ NMR (75 MHz) $\delta$ 173.6, 155.8, 143.4, 139.0, 138.7, 138.5, 136.0, 134.0, 133.4, 131.2, 131.1, 131.0, 130.2, 129.5, 129.1, 129.0, 128.6, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 126.8, 21.5; MS (*m*/*z*, %) 526 ($M^+$, 1.2), 372 (27), 343 (26), 265 (31), 105 (100). Anal. Calcd for $C_{35}H_{26}O_3S$: C, 79.82; H, 4.98. Found: C, 79.62; H, 4.94. The structure was confirmed by X-ray crystallography (see Supporting Information).

Further elution (15% ethyl acetate−hexanes) afforded 85 mg (42%) of 1-benzoyl-1,2-diphenyl-3-(*p*-toluenesulfonyl)-1*H*-indene (**9b**) as white crystals: mp 133−134 °C (from ethyl acetate−hexanes); IR (KBr) 1670, 1443, 1323, 1148 $cm^{-1}$; $^1H$ NMR (400 MHz) $\delta$ 8.39 (d, $J$ = 7.9 Hz, 1H), 7.59 (d, $J$ = 8.2 Hz, 2H), 7.56 (m, 1H), 7.42 (m, 1H), 7.40 (m, 1H), 7.36 (d, $J$ = 7.5 Hz, 2H), 7.34 (m, 1H), 7.26 (d, $J$ = 6.4 Hz, 1H), 7.23 (d, $J$ = 7.1 Hz, 1H), 7.18 (d, $J$ = 8.2 Hz, 2H), 7.14 (d, $J$ = 7.7 Hz, 2H), 7.11 (d, $J$ = 7.6 Hz, 2H), 7.05 (t, $J$ = 7.8 Hz, 2H), 6.65 (d, $J$ = 7.4 Hz, 2H), 6.37 (d, $J$ = 7.7 Hz, 2H), 2.38 (s, 3H); $^{13}C$ NMR (75 MHz) $\delta$ 195.9, 160.3, 144.1, 143.3, 140.6, 140.0, 137.9, 137.3, 136.3, 132.4, 132.2, 129.7, 129.3, 129.1, 129.0, 128.6, 128.2, 128.1, 127.9, 127.8, 127.7, 127.4, 126.6, 125.6, 123.9, 79.5, 21.4; MS (*m*/*z*, %) 526 ($M^+$, 0.7), 371 (73), 265 (53), 105 (100); HRMS calcd for $C_{35}H_{26}O_3S$ ($M^+$), 526.1603; found, 526.1590. Anal. Calcd for $C_{35}H_{26}O_3S$: C, 79.82; H, 4.98. Found: C, 79.47; H, 4.81. See Supporting Information for HMBC and HMQC correlations for **9b**.

**Photolysis of Benzoxepin 8b.** A solution of **8b** (53 mg, 0.10 mmol) in 3 mL of dichloromethane was irradiated for 2 d, as in the preceding experiments. The solvent was evaporated, and the residue was separated by flash chromatography (14% ethyl acetate−hexanes) to afford 21 mg (40%) of recovered **8b**, followed by 29 mg (55%) of **9b**.

**Reactions in the Presence of BHT.** A solution of **4a** (44 mg, 0.087 mmol) and BHT (3.8 mg, 0.017 mmol) in xylenes (2 mL) was heated in a sealed V-vial at 150 °C for 60 h. After the solution was cooled to room temperature, the reaction mixture was concentrated under reduced pressure and dried to afford 48 mg of a yellow solid that contained **5a** and **7a** (vide supra) in the ratio of about 1:1 (NMR analysis).

The above reaction was repeated with **4a** (51 mg, 0.10 mmol) and BHT (44 mg, 0.20 mmol). The product again contained **5a** and **7a** in the ratio of about 1:1 (NMR analysis).

A solution of **4b** (53 mg, 0.10 mmol) and BHT (4.4 mg, 0.020 mmol) in xylenes (2 mL) was heated in a sealed V-vial at 154 °C for 60 h. After the solution was cooled to room temperature, the reaction mixture was concentrated under reduced pressure to afford 57 mg of a yellow solid that contained ketones **5b** and **6b** (vide supra) in the ratio of 1:2.6 (NMR analysis).

The above reaction was repeated with **4b** (39 mg, 0.074 mmol) and BHT (33 mg, 0.15 mmol). The product again contained **5b** and **6b** in the ratio of 1:2.6 (NMR analysis).

**Acknowledgment.** We thank Merck Frosst (Canada), Ltd., and the Natural Sciences and Engineering Research Council of Canada for financial support.

**Supporting Information Available:** X-ray crystallographic data for compounds **4a**, **5a**, **5b**, **6b**, and **8b**, as well as NMR data for **9b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO060598E