Trapping Reactions of 1,3-Bridged Cyclopropenes

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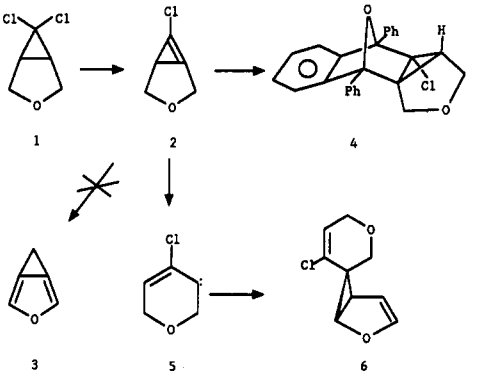
The reactive bicyclo[*n*.1.0]alk-1(ω)-enes (*n* = 3–6) **9a–d** are formed by dehydrochlorination of **8a–d** and trapped by diphenylisobenzofuran as exo Diels–Alder adducts **10a–d**. With **8c** the major adduct, **18** results not from interception of **9c** but from diene **16** that is formed by dehydrochlorination/rearrangement sequences. Attempted interception of cyclopropenes **9a–d** by furan provides a [4 + 2] product **19** from **9b** (*n* = 4) only. Under the conditions employed, **9a** (*n* = 3) ring expands to carbene prior to furan trapping while homologues **9c** and **9d** (*n* > 4) rearrange and lose HCl to give **17** and **20**, respectively, without intervention of furan. 7-Chlorobicyclo[4.1.0]hepta-1(7),3-diene is likewise captured by diphenylisobenzofuran as **13**.

There is much current interest in strained organic molecules,[1] and the synthesis and utilization of cyclopropenes as simple carbocycles[2] as well as part of constrained ring assemblies[3–6] continues to attract attention. Our ongoing study of the cycloproparenes[7] has focused itself recently on nonbenzenoid aromatic species,[8] and the synthesis of cyclopropa[*c*]furan (**3**) was attempted. During this project is was discovered[9] that the 1,3-bridged cyclopropene **2** is intercepted by 1,3-diphenylisobenzofuran (DPIBF) as exo and endo Diels–Alder adducts, e.g. **4** (Scheme I), while furan reacts only with the carbene **5** derived from relief of strain through scission of the bridge bond. The fascination of this "partition trapping" encouraged us to extend these studies to carbocyclic analogues, and we now report upon the behavior of the transient 1,3-bridged cyclopropenes **9a–d** (Scheme II) derived from the ω,ω-dichlorobicyclo[*n*.1.0]alkanes **8** (*n* = 3–6).

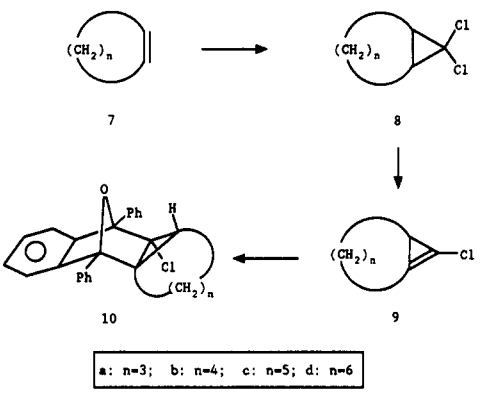
Reaction of **8a–d** with base in the presence of DPIBF leads, at least in part, to capture of **9a–d** as 1:1 adducts. In the case of the bicyclohexene **9a**, a [$_{\pi}2 + _{\pi}4$] adduct was obtained in ca. 14% yield. The compound is assigned as the exo Diels–Alder product **10a** (Scheme II) in analogy to **4**. In particular the ^{1}H NMR spectrum exhibits a typically[9–11] deshielded proton (3.04 ppm) due to the proximity of the cyclopropyl proton to the oxygen bridge; the isomeric endo adduct was not found. In the formation[9] of DPIBF adducts from **2** the exo/endo ratio is ca. 5:1.

Bicycloheptene **9b** has been generated both by vacuum gas–solid reaction[5] and in solution[12] from fluoride ion induced desilylation of the 1-trimethylsilyl equivalent of **8b**. We find that this reactive molecule is easily available from dehydrochlorination of **8b** in either THF or DMSO;

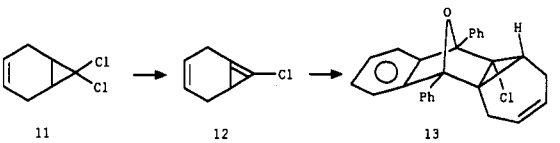
Scheme I



Scheme II



Scheme III



DPIBF trapping gives **10b** (Scheme II) in yields of up to 42%. Chan and Massuda[12] intercepted **9b** as **10b** in 12% yield, and from their report and our own observations the exo addition of DPIBF to **9b** must proceed with high stereoselectivity as no evidence was gleaned for the presence of the isomeric endo product. Furthermore, it is notable that **9b** rearranges upon gas-phase generation,[5] but the structure of the product is apparently not[13] the 2-chlorocyclohepta-1,3-diene originally claimed. Without a trap and in DMSO, **9b** reacts further[14] with excess *tert*-

(1) See, for example: *Chem. Rev.* **1989**, *89* (5). *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI Press: London, 1991; Vol. 1.
(2) Halton, B.; Banwell, M. G. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: Chichester, 1987; Chapter 21, pp 1223–1339. Baird, M. S. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed. JAI Press: London, 1991; Vol. 1, p 65.
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(4) Chenier, P. J.; Southland, D. A. *J. Org. Chem.* **1989**, *54*, 3519.
(5) Billups, W. E.; Lee, G.-A.; Arney, B. E.; Whitmire, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 7980.
(6) Wiberg, K. B.; Artis, D. R.; Bonneville, G. *J. Am. Chem. Soc.* **1991**, *113*, 7969.
(7) Halton, B. *Chem. Rev.* **1989**, *89*, 1161 and references cited.
(8) See, for example: Halton, B.; Russell, S. G. G. *Aust. J. Chem.*, in press.
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(10) Dent, B. R.; Halton, B. *Aust. J. Chem.* **1987**, *40*, 925. Müller, P.; Bernardinelli, G.; Pfyffer, J.; Rodriguez, D.; Schaller, J.-P. *Chimia* **1987**, *41*, 244; *Helv. Chim. Acta* **1988**, *71*, 544. Apeloig, Y.; Arad, D.; Kapon, M.; Wallerstein, M. *Tetrahedron Lett.* **1987**, *28*, 5917.
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(12) Chan, T. H.; Massuda, D. *Tetrahedron Lett.* **1975**, 3383.
(13) Banwell, M. G., private communication, 1992.
(14) Ransom, C. J.; Reese, C. B. *J. Chem. Soc., Chem. Commun.* **1975**, 970.

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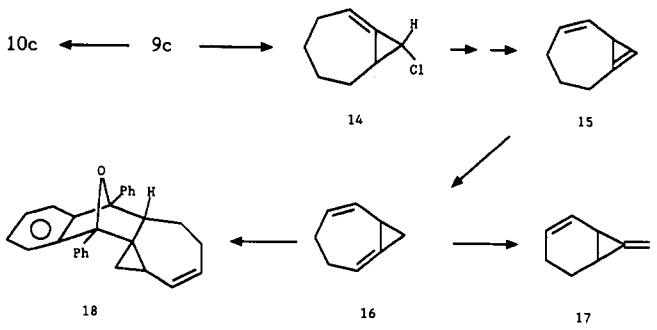
Scheme IV

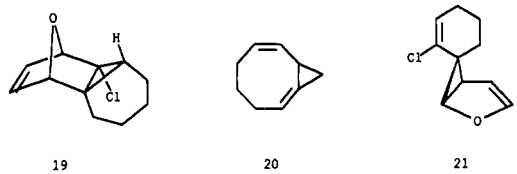


butoxide to give strained 1(7)-alkenes, cf. **9b**, that are stabilized by methyl group incorporation from the solvent; *o*-ethyltoluene and ethylbenzene are the major products.[14] The partial formation of such volatile compounds in the present work would not be detected as excess DPIBF is removed by aerial oxidation to *o*-dibenzoylbenzene.[15]

In analogy with **8b** we find that the bicycloheptene **11**, the precursor to cyclopropabenzene,[7] loses HCl with *tert*-butoxide to give the 1(7),3-diene **12** that is diverted to **13** (25%) with DPIBF (Scheme III). Again the sole cyclopropane proton is deshielded (2.98 ppm) by the proximal oxygen. There is neither addition to the Δ^3-double bond of **12** nor to substrate **11** under the same conditions, the latter in the absence of base. The decidely foul odor of cyclopropabenzene rapidly becomes evident, and the trapping showed that **12** is indeed the primary product of elimination from **11** as proposed[16] in 1971.

Interception of bicyclononene **9d** by DPIBF affords adduct **10d** (16%) (Scheme II) as the only product isolated in addition to *o*-dibenzoylbenzene. By comparison, reaction of **8c** leads to two products. The expected adduct **10c** from **9c** appears in 12% yield while the major product, a non-chlorine-containing compound and also a DPIBF adduct, is isolated in 28% yield. This last compound does not result from adduct **10c** as **10c** is recovered in 81% yield when resubjected to the reaction conditions. Now it is known[17] that didehydrochlorination of **8c** leads to 7-methylenebicyclo[4.1.0]hept-2-ene (**17**) via a methylenecyclopropane rearrangement from **16** as shown in Scheme IV. The possible involvement of **17** in giving the second product is discounted as **17** fails to provide a DPIBF adduct under the conditions employed. The new adduct is identified as **18** that results from trapping **16** across the methylenecyclopropane π-bond. The structure of **18** follows from 2D NMR analyses. In particular, ^1H–^1H COSY reveals that the nonequivalent cyclopropane methylene protons (0.34, 0.60 ppm) are coupled to a methine proton (1.54 ppm) that is in turn connected to a vinylic proton (5.66 ppm). The only other vinylic proton (5.27 ppm) is connected to the methylene of a–$CH_2CH_2CH<$ moiety. Taken together these account for the 7C fragment $-CH_AH_BCHCH{=}CHCH_2CH_2CH-$. The results of ^1H–^{13}C COSY studies compliment fully this analysis. However, the stereochemistry about the spirocyclopropane unit of **18** is not known. (Unfortunately crystals of **18** were not suitable for X-ray analysis.) As the ring junction methine proton of the $-CH_2CH_2CH<$ unit appears at 3.16 ppm, an exo orientation with deshielding by the bridging oxygen is implied. The 2D NMR connectivities displayed clearly exclude cycloaddition to **15**, the ring-stained cyclopropene progenitor of **16**, that might have been deemed more likely; it would seem that π-bond migration to **16** proceeds more rapidly than interception by DPIBF.

In the presence of furan only one of the strained olefins is intercepted, and then in very low yield. Product **19** (3%) exhibits the necessary characteristics for exo Diels–Alder addition to the $\Delta^{1,7}$-double bond of **9b** but with a cyclopropyl proton signal at 2.26 ppm. While this is ca. 0.6 ppm at higher field than in the DPIBF analog **10b**, it is still significantly deshielded by comparison with the endo isomer of **4** (1.60 ppm[9]), and exo orientation is assumed. For the bridged cyclopropenes **9c** and **9d**, furan is an ineffective trap as they react further to give the known[17] dienes **17** (41%) and **20** (61%). In comparison, the more highly strained **9a** reacts by way of bridge bond opening in a manner strictly analogous to that of oxa homologue **2**; spirocycle **21** (ca. 15%) is isolated admixed (ca. 1:3) with starting material **8a**. The data for **21** match those previously reported for the product obtained from 1,2-dechlorination of 1,6,6-trichlorobicyclo[3.1.0]hexane.[18] However, the stereoassignment of **21** is revised to have the chlorine atom exo to the dihydrofuran moiety in strict analogy to **6** where this was firmly established from NOE experiments.[9]



The results show that transient 1,3-bridged cyclopropenes **9** may be detected by DPIBF trapping. Although furan is to be found notably less effective, its use has provided a fascinating insight into the manifestation of strain in these molecules under the basic conditions employed. Thus the three-atom bridge of **9a** and its oxa analogue **2** must act as a pincer on the bridge bond as scission occurs. The rate of reaction is *greater* than that for cycloaddition to furan but *less* than that for reaction with DPIBF. With $n = 4$ **9b** is the least strained of the molecules examined; it has sufficient stability to be detected by addition to both reagents. In comparison, increasing further the size of the bridging unit from four to five or more members, as in **9c** and **9d**, serves not to compress but to stretch the bridge bond. This manifests itself in rearrangement to a methylenecyclopropane, e.g. **14**, that is not trapped but undergoes further rearrangement and dehydrochlorination as shown in Scheme IV.

Experimental Section

For general methods and procedures see ref 9. Column, radial, and thin-layer chromatographies employed silica, Kieselgel 60 PF_{254}, and Kieselgel GF_{254}, respectively, with petroleum ether/dichloromethane (2:1) elution. Infrared spectra were recorded for KBr disks.

Generation and Trapping of the ω-Chlorobicyclo[*n*.1.0]-alk-1(ω)-enes 9 and 13 with 1,3-Diphenylisobenzofuran. To a solution of potassium *tert*-butoxide (ca. 5 molar equiv) and 1,3-diphenylisobenzofuran (DPIBF) (ca. 1 molar equiv) in dry DMSO (or THF) (20 mL) under dry nitrogen at 0 °C was added the appropriate ω,ω-dichlorobicyclo[*n*.1.0]alkane **8** (or **11**, see E below) (ca. 0.5 g, ca. 3.0 mmol) dropwise over 30 min. The mixture was then stirred for 30 min, warmed to room temperature, and stirred for a further 1 h. Water (50 mL) was added, the solution was extracted with dichloromethane (3 × 20 mL), and the separated organic phase was dried ($MgSO_4$) and concentrated in vacuum to a brown solid. Unchanged DPIBF (TLC), was oxidized

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(17) Billups, W. E.; Baker, B. A.; Chow, W. Y.; Leavell, K. H.; Lewis, E. S. *J. Org. Chem.* **1975**, *40*, 1702.
(18) Baird, M. S.; Nethercott, W. *Tetrahedron Lett.* **1983**, *24*, 1983.

to o-dibenzoylbenzene by aeration (for periods exceeding 18 h), and the resultant pale brown solid was subjected to preparative TLC. Bands were extracted with dichloromethane.

A. From 6,6-Dichlorobicyclo[3.1.0]hexane (8a).[19] **8a** (475 mg, 3.15 mmol) in DMSO (or THF) gave two bands from preparative TLC.

Band A (R_f 0.5) gave o-dibenzoylbenzene (DMSO 307 mg, 33%; THF 530 mg, 60%): mp 147–148 °C (lit.[20] mp 147–148 °C).

Band B (R_f 0.75) afforded a yellow powder which gave colorless crystals (dichloromethane) of adduct **10a** (DMSO 185 mg, 14%; THF 55 mg, 4.2%): mp 127–128 °C; ^{1}H NMR δ 1.35–1.44 (m, 1 H), 1.77–1.93 (m, 2 H), 1.96–2.06 (m, 1 H), 2.15–2.36 (m, 2 H), 3.04 (d, J = 5.9 Hz, >CH–), 7.24–7.36 (m, 4 H), 7.39–7.49 (m, 6 H), 7.68 (broad s, 2 H), 7.77 (broad s, 2 H); ^{13}C NMR δ 24.2 (5), 25.4, 27.2 (all CH_2), 39.5 (CH), 51.1 (C), 64.5 (CCl), 88.7, 91.1 (both PhCO), 120.5, 122.7 (5), 126.5, 127.2, 128.2 (5), 128.4, 128.6, 128.8, 129.0, 129.2 (all CH), 133.7, 134.3 (5), 147.5, 148.5 (all C). Anal. Calcd for $C_{26}H_{21}ClO$: C, 81.1; H, 5.5; Cl, 9.2. Found: C, 80.9; H, 5.4; Cl, 9.0.

B. From 7,7-Dichlorobicyclo[4.1.0]heptane (8b).[19] **8b** (500 mg, 3.02 mmol) in ether DMSO or THF gave two bands from preparative TLC.

Band A (R_f 0.55) gave o-dibenzoylbenzene (DMSO 570 mg, 49%; THF 592 mg 51%): mp 147–148 °C (lit.[20] mp 147–148 °C).

Band B (R_f 0.67) gave (dichloromethane) colorless needles of adduct **10b** (DMSO 506 mg, 42%; THF 406 mg, 34%): mp 166–168 °C (lit.[12] mp 166–168 °C).

C. From 8,8-Dichlorobicyclo[5.1.0]octane (8c).[19] **8c** (500 mg, 2.8 mmol) in DMSO gave four bands from preparative TLC.

Band A (R_f 0.35–0.45) yielded o-dibenzoylbenzene (273 mg, 34%): mp 146–147 °C (lit.[20] 147–148 °C).

Band B (R_f 0.62) gave (dichloromethane) colorless crystals of the methylenecyclopropane adduct **18** (287 mg, 28%): mp 160–161 °C; IR 3062, 3005, 2931, 1500, 1446, 1350, 1307, 1009, 978, 904, 762, 742, 709, 686, 659 cm^{-1}; ^{1}H NMR δ 0.34 (dd, J = 4.00, 5.82 Hz, 1 H), 0.60 (d, J = 4.00, 10.01 Hz, 1 H), 0.75–0.88 (m, 1 H), 1.50–1.59 (m, 1 H), 1.87–1.93 (m, 1 H), 2.00 (d, J = 5.59 Hz, 2 H), 3.16 (dd, J = 2.13, 11.26 Hz, 1 H), 5.23–5.31 (m, 1 H), 5.66 (dd, J = 5.51, 11.99 Hz, 1 H), 7.03–7.23 (m, 4 H), 7.31–7.49 (m, 6 H), 7.62–7.65 (m, 2 H), 7.71–7.74 (m, 2 H); ^{13}C NMR δ 17.7 (CH), 21.5, 28.0, 31.2 (all CH_2), 39.4 (C), 52.8 (5) (CH), 89.8, 90.5 (both PhCO), 126.7 (>CHCH=), 129.2, (CH_2CH=), 119.3, 121.4, 125.2 (5), 126.2, 126.7, 127.5, 127.9, 128.2 (5), 128.4, 128.4 (all CH), 136.5, 137.7, 147.1, 147.7 (all C); mass spectrum (70 eV), m/z (relative intensity) 377/376 (8/24, M), 349/348 (4/14, M – C_5H_7), 271/270 (38/100, M – C_8H_{10}). Anal. Calcd for $C_{28}H_{24}O$: C, 89.3; H, 6.4. Found: C, 89.3; H, 6.6.

Band C (R_f 0.69) afforded a white solid (173 mg) thought to consist of a mixture of **18** and an isomer together with **10c** (see below).

Band D (R_f 0.74) provided colorless crystals (dichloromethane) of Diels–Alder adduct **10c** (172 mg, 12%): mp 126–127 °C; ^{1}H NMR δ 1.14–1.16 (m, 5 H), 1.75–1.90 (m, 4 H), 2.15–2.23 (m, 1 H), 2.85 (dd, J = 7.2, 10.6 Hz, >CH–), 7.15–7.30 (m, 4 H), 7.35–7.55 (m, 6 H), 7.6–7.7 (m, 2 H), 7.75–7.80 (m, 2 H); ^{13}C NMR δ 25.5 (5), 27.3, 27.4, 28.3, 32.8 (all CH_2), 34.1 (CH), 42.2 (C), 65.4 (CCl), 89.7, 89.8 (both PhCO), 121.4, 122.7, 126.2, 126.3, 126.9, 128.2, 128.3, 128.5, 128.9, 129.2 (all CH), 134.0, 136.2, 147.2, 148.6 (all C); mass spectrum (70 eV), m/z (relative intensity) 378/377 (30/100, M – Cl), 271/270 (5/13, M – $C_8H_{11}Cl$). Anal. Calcd for $C_{28}H_{25}ClO$: C, 81.4; H, 6.1; Cl, 8.6. Found: C, 81.0; H, 5.8; Cl, 8.7.

Resubjection of Diels–Alder adduct **10c** (170 mg, 0.42 mmol) to an excess of KOBu-t (234 mg, 2.1 mmol) in DMSO as described above resulted in the recovery of **10c** (141 mg, 81%); no evidence was obtained to support the formation of **18** from **10c**.

D. From 9,9-Dichlorobicyclo[6.1.0]nonane (8d).[19] **8d** (600 mg, 3.11 mmol) in DMSO gave two bands from preparative TLC.

Band A (R_f 0.6–0.7) yielded o-dibenzoylbenzene (606 mg, 68%): mp 147–148 °C (lit.[20] mp 147–148 °C).

Band B (R_f 0.75–0.85) gave colorless crystals (dichloromethane) of adduct **10d** (211 mg, 16%): mp 156–158 °C; IR 3039, 2919, 2859, 1499, 1465, 1446, 1344, 1299, 1011, 991, 764, 753, 703, 556 cm^{-1}; ^{1}H NMR δ 0.92–1.45 (m, 9 H), 1.49 (d, J = 4.0 Hz, 1 H), 1.60–1.65 (m, 1 H), 1.96–2.05 (m, 1 H), 2.59 (dd, J = 3.1, 11.6 Hz, >CH–), 7.23–7.32 (m, 4 H), 7.36–7.51 (m, 6 H), 7.69–7.77 (m, 2 H), 7.83–7.88 (m, 2 H); ^{13}C NMR δ 23.8, 25.6, 26.1, 26.8, 27.7 (all CH_2), 24.4 (5) (>$CHCH_2$), 31.9 (>$CHCH_2$), 40.1 (C), 61.8 (CCl), 89.4, 89.9 (both PhCO), 121.8, 122.7, 126.2 (5), 126.3, 126.6, 128.1, 128.1, 128.5, 129.0, 129.4 (all CH), 134.0, 137.4, 147.1, 148.3 (all C); mass spectrum (70 eV), m/z (relative intensity) 392/391 (31/100, M – Cl), 271/270 (5.5/21, M – $C_9H_{13}Cl$). Anal. Calcd for $C_{29}H_{27}ClO$: C, 81.6; H, 6.4; Cl, 8.3). Found: C, 81.6; H, 6.4(5); Cl, 8.5.

E. From 7,7-Dichlorobicyclo[4.1.0]hept-3-ene (12).[16] **11** (440 mg, 2.75 mmol) in DMSO evolved the malodor of bicyclo-[4.1.0]hepta-1,3,5-triene (cyclopropabenzene). Upon preparative TLC two bands were isolated.

Band A (R_f 0.4–0.5) yielded o-dibenzoylbenzene (491 mg, 62%): mp 147–148 °C (lit.[20] mp 147–148 °C).

Band B (R_f 0.51–0.62) gave adduct **13** (270 mg, 25%) as colorless crystals (dichloromethane): mp 149–150 °C; IR 3039, 2977, 2892, 2830, 1457, 1448, 1301, 1051, 994, 984, 741, 749, 702, 668, 642, 588 cm^{-1}; ^{1}H NMR 1.26–1.40 (m, 1 H), 2.27–2.36 (m, 1 H), 2.44–2.53 (m, 1 H), 2.73–2.84 (m, 1 H), 2.96–2.99 (d, J = 7.95 Hz, >CH–), 5.5–5.6 (m, CH=), 5.66–5.71 (m, CH=), 7.20–7.34 (m, 4 H), 7.40–7.53 (m, 6 H), 7.60–7.63 (m, 2 H), 7.74–7.78 (m, 2 H); ^{13}C NMR δ 20.1 (=$CHCH_2$C), 21.8 (5) (>$CHCH_2$CH=), 25.8 (>CH–), 32.7(C), 61.0, (CCl), 90.8, 90.85 (both PhCO), 122.7, 124.0 (5) (CH_2CH=$CHCH_2$), 121.2, 122.4, 126.5, 126.6, 128.4 (5), 128.7, 128.9 (5), 129.0, 129.2, 129.3 (all CH), 133.8, 133.9, 147.3, 148.0 (all C); mass spectrum (70 eV), m/z (relative intensity) 397/396 (1.1/4.3, M), 362/361 (28/100, M – Cl), 271/270 (7/20, M – C_7H_7Cl). Anal. Calcd for $C_{29}H_{27}ClO$: C, 81.7; H, 5.3; Cl, 8.9. Found: C, 81.9; H, 5.5; Cl, 8.8. In the absence of KOBu-t, substrate **11** does not react; o-dibenzoylbenzene (from DPIBF) was isolated in 83% yield.

Generation and Trapping of the ω-Chlorobicyclo[*n*.1.0]alk-1(ω)-enes 9 with Furan. To a solution of potassium *tert*-butoxide (5–6 molar equiv) in THF (60 mL) under a dry nitrogen atmosphere and at 0 °C was added dropwise over 30–45 min the appropriate ω,ω-dichlorobicyclo[*n*.1.0]alkane **8** (ca. 5 g, ca. 30 mmol) in furan (25 mL). The mixture was stirred at 0 °C for 60 min, allowed to warm to room temperature, and stirred for a further 24–48 h. Excess furan was removed in vacuum, water (50 mL) was added, and the mixture was extracted with dichloromethane (3 × 20 mL). The separated organic phase was dried ($MgSO_4$) and concentrated in vacuum to a brown oil that was subjected to column chromatography.

A. From 6,6-Dichlorobicyclo[3.1.0]hexane (8a).[19] **8a** (5.0 g, 33 mmol) led to a yellow oil (153 mg) shown by ^{1}H NMR to consist of a ca. 85:15 mixture of unchanged starting material and carbene adduct **21** (see below). Careful rechromatography provided a fraction enriched in **21** (**8a**:**21** ca. 3:1), the NMR spectra of which showed NMR resonances fully in accord with those previously[18] reported for **21**. The exclusion of THF as diluent or the use of DMSO as solvent resulted in no adduct formation.

B. From 7,7-Dichlorobicyclo[4.1.0]heptane[19] **(8b). 8b** (5 g, 30 mmol) gave unchanged starting material (1.83 g, 37%) and an oil (203 mg) from column chromatography. The oil, purified by preparative TLC (R_f 0.3), is identified as Diels–Alder adduct **19** (188 mg, 3%) (the compound discolored prior to the aquisition of microanalytical data): ^{1}H NMR δ 1.17–1.41 (m, 5 H), 1.47–1.53 (m, 1 H), 1.75–1.84 (m, 1 H), 1.92–2.03 (m, 1 H), 2.26 (dd, J = 8.9, 2.4, >CH–), 4.47 (s, CHO), 4.75 (s, CHO), 6.64 (s, 2 CH=); ^{13}C NMR δ 19.6, 20.9, 21.0, 21.3 (5) (all CH_2), 27.1 (CH), 31.7 (5) (C), 60.4 (CCl), 81.8, 82.4 (both HCO), 137.7, 138.1 (5) (both CH=); mass spectrum (70 eV), m/z (relative intensity) 167 (31, M – CHO), 161 (35, M – Cl), 127/125 (39/100, C_7H_6Cl), 91 (77, C_7H_7); exact mass calcd for $C_{10}H_{12}{}^{35}Cl$ m/z 167.0628 and for $C_{11}H_{13}$ m/z 161.0966, found m/z 167.0629 and 161.0963, respectively. On using DMSO as solvent the yield of **19** fell to ca. 0.5%.

C. From 8,8-Dichlorobicyclo[5.1.0]octane (8c).[19] **8c** (5 g, 28 mmol) with furan in the presence or absence of THF returned unchanged starting material in yields of up to 43%; no other products were detected. The reaction was then performed by adding a solution of **8c** and furan (20 mL) to the base in DMSO (25 mL) (as described for the reactions with DPIBF above),

(19) Bergman, E. *J. Org. Chem.* **1963**, *28*, 2210.
(20) *Dictionary of Organic Compounds*, 5th ed.; Eyre & Spotswoode: London, 1965.

whereupon a homogeneous pale brown oil was isolated. The product is identified as the previously reported[17] 7-methylenebicyclo[4.1.0]hept-2-ene (17) (1.23 g, 41%), identical to a sample prepared independently: ^{1}H NMR δ 0.85–2.2 (m, 6 H), 5.2–6.2 (m, 4 H); ^{13}C NMR[21] δ 15.0, 17.2 (C1/C6), 17.0, 21.1 (C5/C4), 103.0 (=CH_2), 124.0, 126.0 (C2/C3), 135.7 (C7). No evidence was obtained to support the formation of [4 + 2] adduct.

D. From 9,9-Dichlorobicyclo[6.1.0]nonane (8d).[19] **8d** (5 g, 26 mmol) with furan gave one fraction from column chromatography that provided spectroscopic data identical to those reported[17] for bicyclo[6.1.0]nona-1,6-diene (**20**) (1.7 g, 61%). No evidence was obtained for the formation of a [4 + 2] adduct.

(21) The earlier report (see ref 16) quotes eight distinct signals for 17 but does not give the chemical shifts.

7-Methylenebicyclo[4.1.0]hept-2-ene (17). This was prepared from **8c** (1.0 g, 5.6 mmol) according to the method of Billups et al.[17] Yield: 185 mg, 31% (lit.[17] 42%). The compound was identical to that obtained in the presence of furan.

Attempted Addition of 7-Methylenebicyclo[4.1.0]hept-2-ene (17) to 1,3-Diphenylisobenzofuran. Reaction of **17** (120 mg, 1.1 mmol) with DPIBF (300 mg, 1.1 mmol) in DMSO (25 mL) as described for **9** above gave, as the only characterizable product, *o*-dibenzoylbenzene (262 mg, 83%), mp 146–147 °C (lit.[20] mp 147–148 °C).

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Diels–Alder Cycloadditions Using Nucleophilic 3-(*p*-Tolylthio)-2-pyrone. Regiocontrolled and Stereocontrolled Synthesis of Unsaturated, Bridged, Bicyclic Lactones

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Captodative 3-(tolylthio)-2-pyrone (1) is shown to be reactive as a nucleophilic diene undergoing 2 + 4-cycloadditions with various electrophilic alkenes under sufficiently *mild thermal conditions* (≤90 °C) so that the initial bicyclic lactone adducts can be isolated on gram scale in moderate to very good yields (42–82%) *without loss of* CO_2. These bicyclic adducts are formed regiospecifically and often with excellent stereoselectivity. These Diels–Alder cycloadditions are *the first examples of a captodative unsaturated sulfide acting as an enophile.* NMR data (^{13}C) are presented correlating the electron density in the pyrone diene systems with their Diels–Alder reactivity, and some transformations of the bicyclic lactone adducts are shown to illustrate the value and versatility of these richly functionalized synthetic intermediates.

Introduction

Typically, 2-pyrones cycloadd to various alkenes at temperatures so high (~100–200 °C) that loss of CO_2 from the initial bicyclic lactone adducts occurs in situ.[1] Attempts to isolate these initial nonaromatic bicyclic adducts generally have failed. Some exceptions exist.[2] For example, 3-hydroxy-2-pyrone has been reported to undergo thermal and high-pressure cycloadditions with maleic anhydride and with acrylate and acrylonitrile derivatives, and the bicycloadducts have been isolated but without characterization of their stereochemistry; in several instances, these bicycloadducts decomposed on attempted chromatographic purification.[3] Also, carboxylate esters of 3-hydroxy-2-pyrone have been reported to undergo high-pressure, stereoselective, inverse-electron-demand cycloaddition with electron-rich vinyl ethers,[4] and pyrone itself has been reported to undergo some cycloadditions with alkenes at 19 kbar.[5] Because unsaturated, bridged, bicyclic lactones are structurally rich and versatile building units having fixed and useful stereochemical relationships, we have sought simple and direct ways to synthesize these valuable compounds. Success has been achieved using *electrophilic* 3-sulfinyl- and especially 3-sulfonyl-2-pyrones that reliably undergo mild and stereocontrolled 2 + 4-cycloadditions with nucleophilic dienophiles such as enol ethers.[6] The stable bicyclic lactones so formed have served effectively as key polyfunctional building units in construction of shikimate,[7] chorismate,[8] and vitamin D_3 de-

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