HOAc (60 mL) for 6 h. The reaction was poured into $Na_2S_2O_5$ solution, and the precipitate collected by filtration was purified by chromatography on silica with benzene as eluant to give **40**: 1.23 g (97%); pale yellow leaflets (ligroin), mp 192–193 °C (lit.[21] mp 192.5–193.5 °C); ^1H NMR ($CDCl_3$) δ 3.40 (br s, 4 H, ethano), 8.44 (d, 1 H, H_1), 9.06 (s, 1 H, H_{12}).

Benz[*k*]acephenanthrylene (36). A mixture of compound **40** (1.0 g) and DDQ (1.0 g) in dry xylene (80 mL) was heated at reflux for 20 h. The cooled solution was filtered and the filtrate passed through a column of alumina. Elution by benzene–hexane (1:1) and collection of the yellow non-fluorescent band afforded benz[*k*]acephenanthrylene (**36**): 685 mg (69%); yellowish orange plates (hexane), mp 233–234 °C; UV (hexane) λ_{max} ($\epsilon \times 10^4$) 416 (0.80), 395 (0.12), 352 (1.01), 340 (1.18), 310 (3.60), 297 (1.98), 265 (sh, 4.10), 257 (5.04) nm; accurate mass of molecular ion, 252.0951 (calcd for $C_{20}H_{12}$, 252.0939); major fragments at m/z 252 ($M^{+\cdot}$), 250 ($(M - H_2)^{+}$), 126 (M^{2+}), 125 ($(M - H2)^{2+}$); ^1H NMR (250 MHz, CD_2Cl_2) δ 7.11 (d, 1 H, J = 4.5 Hz, etheno H), 7.26 (d, 1 H, J = 4.5 Hz, etheno H), 8.11 (s, 1 H, K- region H_6), 8.49 (dd, 1 H, J = 8 Hz, 2.5 Hz, bay regionm H_1), 8.54 (s, 1 H, peri H_7), 9.14 (s, 1 H, bay region peri H_{12}), 7.6–8.3 (m, 6 H, remaining Ar H).

Acknowledgment. This work was supproted by USPHS Grant No. CA 28622 and American Cancer Society Grant No. BC388.

Registry No. **3**, 13728-56-8; **4**, 5472-20-8; **5**, 85319-66-0; *endo*-**6**, 13728-59-1; *exo*-**6**, 85319-67-1; **7**, 13728-60-4; **8**, 13728-58-0; **9**, 13728-49-9; **10**, 85319-68-2; **11**, 202-33-5; **12**, 6325-54-8; **13**, 63018-69-9; **14**, 20316-12-5; **15**, 85319-69-3; **16**, 85319-70-6; **17**, 85319-71-7; **18**, 85319-72-8; **19**, 199-54-2; **20**, 1470-04-8; **21**, 85319-73-9; *exo*-**22**, 85319-74-0; *endo*-**22**, 85319-75-1; **23**, 85319-76-2; **24**, 85319-77-3; **25**, 85319-78-4; **26**, 85319-79-5; **27**, 211-91-6; **28**, 35187-29-2; **29**, 58024-08-1; **30**, 2319-96-2; **31**, 85319-80-8; **32**, 85319-81-9; **33**, 85319-82-0; **34**, 85319-83-1; **35**, 85319-84-2; **36**, 212-41-9; **37**, 4623-31-8; **38**, 85319-85-3; **40**, 5779-79-3; ethyl bromoacetate, 105-36-2.

Supplementary Material Available: NMR spectra of compounds **11**, **19**, **27**, and **36** (4 pages). Ordering information is given on any current masthead page.

Regioselective Catalytic Transfer Hydrogenation of Dimethyl Bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, Dimethyl Bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate, and Related Compounds over Palladium on Carbon

Derrick C. Tabor, Franklin H. White, L. Warren Collier, IV, and Slayton A. Evans, Jr.*

The William Rand Kenan, Jr., Laboratories of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514

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The catalytic transfer hydrogenation (CTH) of dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**3**) on palladium on carbon is highly regioselective, giving predominant reduction at the least-substituted olefinic site. The CTH of dimethyl bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate also occurs with exclusive suprafacial exo addition of hydrogen to afford the endo isomer. An increase in the relative concentration of palladium on carbon (ca. 40–45 wt/wt % based on the acceptor) accelerates the rate of CTH while the substituted cyclohexenes undergo CTH faster than cyclohexene with dimethyl bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate.

The catalytic transfer hydrogenation (CTH) process[1] utilizes organic molecules of relatively low oxidation potential as hydrogen donors, DH_n, in the presence of solubilized catalysts (e.g., Ru,[2] Rh,[3] Pd[3b,c]) and heterogeneous metal catalysts (e.g., Pd,[4] Ni[5]) to effect hydrogen transfer to an organic substrate or "acceptor" (A, eq 1).

$$DH_n + A \xrightarrow[\text{solvent}]{\text{catalyst}} AH_2 + DH_{n-2} \quad (1)$$

The CTH process has received considerable recent attention as a useful synthetic method for the reduction of carbonyl compounds[6] and highly substituted olefins[7] as well as hydrogenolysis of "protected" peptides[8] and carbohydrates.[9] While there exists a variety of donor molecules capable of transferring hydrogen atoms to acceptor molecules with varying degrees of efficiency, cyclohexene (**1**), 1,3-cyclohexadiene (**2**), and their alkylated derivatives exhibit a relatively high propensity for hydrogen transfer in the presence of palladium black and palladium on

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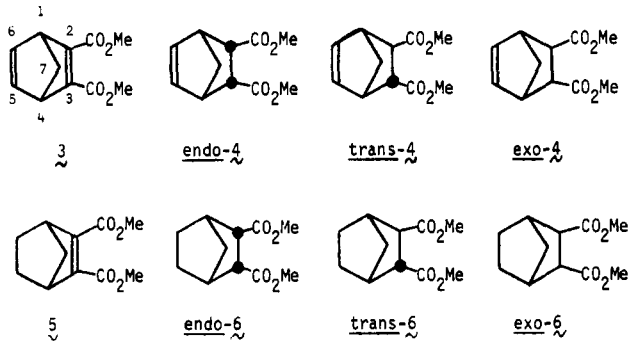
(9) (a) Hanessian, S.; Liak, T. J.; Vanasse, B. *Synthesis* **1981**, 396–7. (b) Rao, V. S.; Perlin, A. S. *Carbohydr. Res.* **1980**, *83*, 175–7.

0022-3263/83/1948-1638$01.50/0

Chart I



carbon.[1] The popularity of these donors reflects their commercial availability, overall effectiveness, and general convenience in handling.

Actually, little is known about the mechanism(s) of these reductions although a number of postulates have been advanced.[10-12] A relatively long-standing view suggested by Linstead et al.[11] and supported by the results of other investigators[12,13] indicates that the transfer of hydrogen between the donor and acceptor molecules is a "linked" process involving a catalyst-mediated donor–acceptor complex rather than a sequence of simple "dehydrogenation–hydrogenation" steps. While there is considerable evidence to support a "linked" transfer process, the general issue has not been satisfactorily resolved.

Our efforts in this area centered on the identification of donors that would afford mild and highly regioselective "reductive discrimination" or "molecular queueing"[14] between two or more olefinic sites within a molecule. A suitable acceptor substrate for our studies had to possess the following: (i) it would have to have two chemically distinct olefinic linkages to allow for determinations of regioselectivity, (ii) at least one of these olefinic sites should be appropriately substituted to allow for the detection of the stereochemistry of hydrogen transfer, and (iii) the substrate and its reduced derivatives should be devoid of conformational flexibility so that stereochemical interpretations are not hampered by conformational mobility. Dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**3**, Chart I) possesses these criteria and was viewed as a suitable substrate for study.[15] The ring strain of the olefinic bonds in **3** should also enhance their reactivity toward catalytic transfer hydrogenation.[16]

In principle, reduction of **3** can occur at the C2–C3 and/or C5–C6 π bonds to afford **4** and **5**, respectively. The relative distribution of products, **4** and **5**, would shed light on the regioselectivity of the CTH process while the relative distribution of **4** and/or **6** (i.e., endo, exo, trans) would provide insight into the stereochemical nature of the transfer process.

Results and Discussion

We have investigated the CTH of norbornadiene diester **3** using a variety of hydrocarbon donors in the presence of palladium on carbon (Pd/C; Table I). Nearly all of the

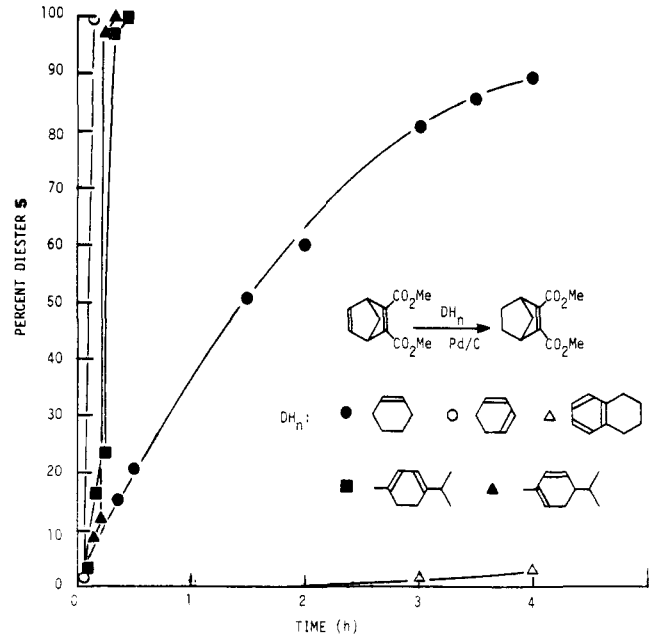
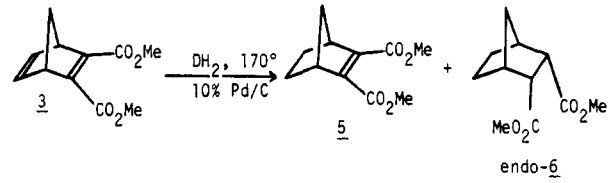


Figure 1. Catalytic transfer hydrogenation of dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate with various donors.

donors examined here effect complete conversion of diester **3** to diester **5** or a mixture of esters **5** and *endo*-**6** (17–37



h) in refluxing (ca. 170 °C) cumene solvent. While tetralin (**7**) and *d*-limonene (**8**) exhibit a suppressed reactivity toward **3**, they are highly regioselective, reacting largely at the C5–C6 olefinic bond to give diester **5**. A donor–acceptor (D/A) ratio between 5 and 7 ensures nearly quantitative reduction of **3** (Table I). This ratio appears necessary to offset loss of donor caused by competitive disproportionation[11,17] on the palladium catalyst.

A measure of the rapidity of the CTH of **3** is obtained by examination of the time-dependent reduction of the C5–C6 π bond by selected donors (Figure 1). The oxidation potentials of the 1,3-cyclohexadienes are generally lower than those for the cyclohexenes, and it is anticipated that they might show increased reactivity. The C5–C6 olefinic bond is quantitatively reduced in 3 min with diene **2** while the diastereoisomeric 1,3-dienes α-phellandrene (**9**) and α-terpinene (**10**) are slower than diene **2** by a factor of 5 and 8, respectively. Cyclohexene requires 4 h to effect 90% reduction of the C5–C6 olefinic bond while *d*-limonene and tetralin are essentially unreactive toward **3** over a 3-h period. The lack of significant reactivity of **7** toward **3** probably reflects a more competitive adsorption of tetralin through the aromatic π system to effectively "poison" the palladium surface, preventing the prerequisite absorption and subsequent activation of diene **3**. This seems reasonable since the molar heats of adsorption for benzene (ΔH_a° = −9.3 kcal/mol) and cyclohexene (ΔH_a° = −5.2 kcal/mol) show that benzene is more strongly chemisorbed than cyclohexene.[17a] *d*-Limonene may preferentially chemisorb through the more accessible terminal olefin

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(11) Braude, E. A.; Linstead, R. P.; Mitchell, P. W. D. *J. Chem. Soc.* **1954**, 3578.
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(15) Hoffmann has shown that there is substantial interaction between the two olefinic bonds (Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1–9). This would imply that while our model compound **3** has two chemically distinct olefinic bonds, they are not necessarily "noninteracting".
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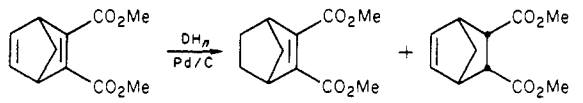
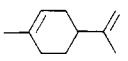
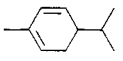
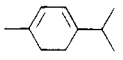
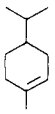
Table I. Catalytic Transfer Hydrogenation (CTH) of Dimethyl Bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (3) with Various Hydrocarbon Donors[a]



3 5 *endo*-4

donor (DH_n)	DH_n/3 molar ratio	time, h	% conversion (% material balance)[b]	product distribution, % 5	product distribution, % *endo*-4	yield,[c] %
 1	5	37	>99	64	36	
	7	22	>99	88	12	56
 2	5	37	>99	98	2	
	7	22	>99	98	2	52
 7	5	22	50	>99	<1	90
 8	7	32	30	>99	<1	48
 9	66	22	>99	24-26	74-76	55
 10	6	17	>99	12	88	66 (72)[d]
 12	6	29	>99	27	73	60
 14	5	22	>99	50	50	92

[a] Reaction conditions: refluxing cumene solvent (10 mL) containing diene 3 (3 mmol) and 10% palladium on carbon (1.1-1.4 mol of Pd). [b] Percent conversion determined by ^1H NMR and/or GLC analyses. [c] Isolated yield of distilled product mixtures based on diene 3. [d] Extended reflux time.

rather than through the C1–C2 olefin bond and therefore discourage metal-mediated hydrogen transfer from the ring hydrogens.[18]

It seems clear from Figure 1 that alkyl substitution within both series of donors causes a notable diminution in the rate of CTH of diene 3. Steric encumbrance caused by alkyl substitution would be expected to alter the relative ease of chemisorption of the organic donor on the catalyst's surface and effectively reduce the reactivity of the donor molecules.[1] Some similarities in the CTH trends involving substituted cyclohexenes and similarly substituted 1,3-cyclohexadienes are expected since the more reactive 1,3-cyclohexadienes are possible intermediates in CTH reactions involving cyclohexenes. 1,3-Cyclohexadiene is more reactive than 1 by an average factor of 31.[17a]

Stereochemistry of the CTH of 3. Conventional hydrogenation procedures applied to the reduction of 2,5-norbornadiene derivatives[19] afford products arising primarily from exo addition of hydrogen. All of the CTH reactions involving 3 and various donors afford endo diester 6 but no trans or exo diester. We conclude that exclusive suprafacial exo addition of hydrogen and no antarafacial addition occurs during the CTH of the norbornadiene skeleton. Actually, this experimental result is expected provided catalytic transfer addition occurs from the sterically least inhibited exo face of the double bond. The different structural features as well as oxidation potentials[1] of the various donors exert no noticeable perturbation during the CTH process that could be reflected in the stereochemistry of the resultant product.

It has been previously shown that catalytic hydrogenation of conformationally rigid olefins and dienes employing both homogeneous[20] and heterogeneous catalysts[21] or carried out in strongly acidic media[22] give products reflecting antarafacial (trans) addition of hydrogen to the olefinic bond. Attempts to alter the stereochemical outcome of the CTH of 3 by addition of trifluoroacetic acid (TFA) to the cumene solution were unsuccessful. The temperatures (155–170 °C) required for effective CTH of 3 were also responsible for the effective demethylation of 3 by TFA.[23]

Effect of Catalyst Concentration on CTH of Diester 3. We attempted the CTH of 3 using donor 1 [1:1, 1:2, and

(18) See, for example: Newhall, W. F. *J. Org. Chem.* **1958**, *23*, 1274.
(19) See, for example: Wiess, R. G.; Snyder, E. I. *J. Org. Chem.* **1970**, *35*, 1627–32.
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(23) Tabor, D. C.; Evans, S. A., Jr. *Synth. Commun.* **1982**, *12*, 855–864.

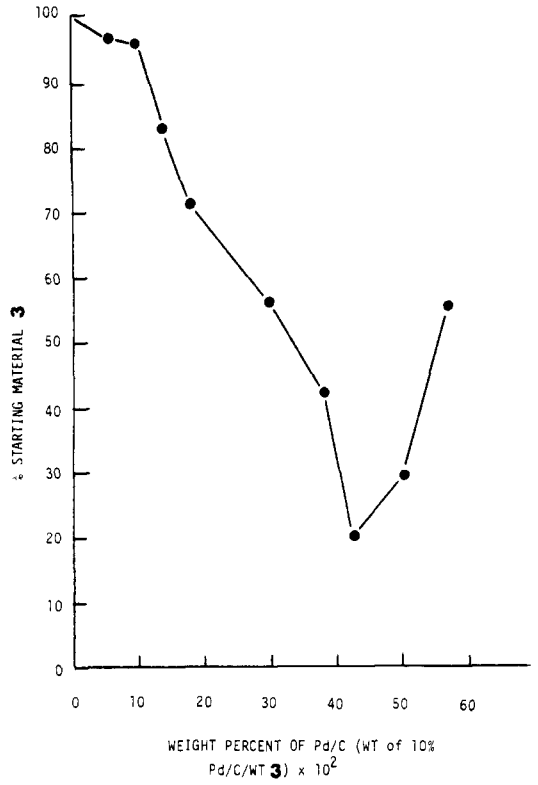


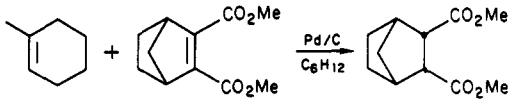
Figure 2. Effect of catalyst concentration of the CTH of dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate.

2:1 molar ratios of 1/3 over 2.5% palladium on carbon (based on the weight of 3) with heating for 13 h in a sealed tube] and observed no reduction. When the reaction containing a 2:1 molar ratio of 1/3 was repeated, varying only the weight percent of Pd/C (2.5–57% based on the weight of 3), the curve shown in Figure 2 was obtained when the percent CTH is plotted against percent catalyst. The curve shows that maximum reduction of the C5–C6 double bond in 3 occurs within 13 h at approximately 40% catalyst weight percent based on 3. The inflection observed in the catalyst-reduction profile may be best rationalized in terms of the decreased proximity between chemisorbed donor and acceptor molecules. As the total palladium surface area required for reaction increases, the probability for "effective" donor–acceptor interactions at the surface with the appropriate orientation suitable for reaction tends to decrease.[24]

Variation of Donor Concentration in CTH of Dimethyl Bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (5). We have examined the concentration dependence of 1-methylcyclohexene (12) in the CTH of dimethyl bicyclo-[2.2.1]hept-2-ene-2,3-dicarboxylate (5). The results (Table II) show that with an equimolar concentration of donor 12 and norbornene 5, 80% CTH can be achieved in 2.25 h. When the D/A ratio is increased slightly to 1.5, the hydrogen-transfer process is complete in less than one-fifth the previous time. When the D/A ratio is 2, the reduction is essentially complete in 9 *min*, and, remarkably, in the absence of cyclohexane solvent (D/A = 1.7), complete reduction occurs in 2 min! It is clear that here, too, exo reduction is preferred, and the CTH process is accelerated by the increase in available donor hydrogens.

Effect of Alkyl Substitution of Donor Reactivity in the CTH of Bicyclo[2.2.1]hept-2-ene (11) and

Table II. Effect of 1-Methylcyclohexene Concentration on the CTH of Dimethyl Bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (5)



12 5 *endo*-6

run	mmol of donor 12 (D)	mmol of acceptor 5 (A)	D/A ratio	mL of solvent[a]	max % CTH (time, min)
A	2.0	2.0	1.0	1.4	80 (135)
B	3.0	2.0	1.5	1.4	99 (20–40)[b,c]
C	4.0	2.0	2.0	1.2	>99 (9)
D	3.5	2.0	1.7		>99 (2)[d]

[a] Cyclohexane is the solvent, and the reactions were performed at 140 °C by using 213 mg of 10% palladium on carbon in each experiment. [b] Purified *endo*-6 was isolated in 93% yield. [c] The CTH of 5 is 94% complete after 20 min by GLC analysis. [d] 1-Methylcyclohexene is used as the solvent as well as the donor in this experiment.

***endo*-Dimethyl Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (*endo*-4).** We have examined the efficiency of cyclohexene, 1-methylcyclohexene (12), and 1-methyl-4-*tert*-butylcyclohexene (13) in the CTH of bicyclo-[2.2.1]hept-2-ene (11) employing a D/A = 0.5 over Pd/C (44% based on the weight of 11) in cyclohexane solvent at 102 °C. Cyclohexene is the most reactive donor, affording 85% reduction after 4.3 h. After 12 h, only 29% reduction (11 → norbornane) had occurred with donor 12; donor 13 gave only 1% norbornane (GLC analysis) after 17 h. It is apparent that the reactivity of the donors decreases substantially as the steric environment at C1 and C4 increases. A similar trend in donor reactivity of 1-substituted cyclohexenes has been observed in the CTH of maleic and cinnamic acids over 5% Pd/C.[25]

The percentage of toluene produced during the reaction of 1-methylcyclohexene (12) and acceptor 11 is equivalent to the amount of norbornane produced. This result shows that disproportionation is not important under the experimental conditions described here and implies that CTH is not a simple dehydrogenation–hydrogenation process. If independent loss of hydrogen were important, formation of toluene should exceed that of norbornane. The fact that the relative amounts are essentially identical lends support to the proposed "linked" hydrogen process. Donor 13 is essentially unreactive toward 11 and apparently does not undergo disproportionation either.

The superior reducing ability of cyclohexene in these systems is further illustrated by comparing the CTH of *endo*-dimethyl bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (*endo*-4) with donors 1, 12, 13, and 1-methyl-4-isopropylcyclohexene (14) at 110 °C in the absence of solvent. A D/A = 0.5 provides two hydrogens for each olefinic acceptor on using 25% active Pd/C, based on the weight of *endo*-4. After 15 min, 83% endo diester 4 is converted into endo diester 6 with donor 1 but <10% CTH of *endo*-4 occurs with 1-methylcyclohexene. 1-Methyl-4-isopropylcyclohexene and 1-methyl-4-*tert*-butylcyclohexene are completely unreactive.

CTH of Dimethyl Bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (5). We have also examined the CTH of dimethyl bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (5)

(24) For a brief discussion on the effect of palladium concentration on the disproportionation of cyclohexene, see ref 12.

(25) (a) Giaffe, A.; Plotiau, A. *C. R. Hebd. Seances Acad. Sci.* **1965**, *261*, 164–6. (b) Scribe, P.; Pallaud, R. *Ibid.* **1963**, *256*, 1120.

with 1 and the same 1-methylcyclohexenes discussed above [2.0 mmol of **5**; 4.0 mmol of donor with 50% Pd/C (wt/wt % based on **5**); 110 °C], and the results are in contrast to those found for the CTH of *endo*-**4**. For example, cyclohexene is the least effective in the CTH of diester **5**, giving 17% *endo*-**6** after 5 min as well as a considerable quantity of benzene (GLC), indicating that disproportionation is more facile than CTH. The CTH of **5** is >95% complete after 10 min when 1-methylcyclohexene is the donor, and when donors **13** and **14** are used, reduction of **5** is complete (>99%) within *1 min*! An interesting contrast is the failure of donor **13** to reduce either the C2–C3 or C5–C6 double bond in diester **3** under the same conditions employed here.

Assuming that the rates of CTH are contingent not only on the proximity of chemisorbed donor and acceptor but also on the position of the chemisorption equilibrium (i.e., relative strength of adsorption) for each, the differences in CTH reactivity between *endo*-**4** or **11** and **5** may be rationalized in the following manner. Apparently, the C2–C3 double bond in **11** or the C5–C6 olefinic bond in *endo*-**4** and cyclohexene is strongly chemisorbed and therefore promotes a more efficienct CTH reaction. The more substituted cyclohexenes are not chemisorbed as strongly because of steric interference caused by the alkyl substituent (s). If the position of the chemisorption equilibrium for cyclohexene on Pd/C indicates strong chemisorption, this would limit chemisorption of weakly chemisorbed **5** and increase the propensity for disproportionation of **1**. Presently we are not prepared to provide a quantitative explanation for the striking increase in reactivity of the substituted cyclohexenes toward diester **5**. Nevertheless, these results may have useful synthetic potential especially for the rapid reduction of α,β-unsaturated carbonyl compounds.

Experimental Section

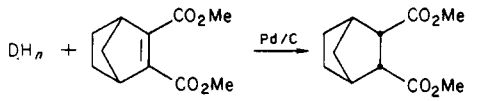
Melting points were obtained in a Mel-Temp melting point apparatus with an open capillary tube and are uncorrected. ^{1}H NMR spectra were recorded on JEOL (60-MHz), Hitachi Perkin-Elmer Model R24-B (high-resolution, 60-MHz), and Varian Model XL-100-12 (100 MHz) NMR spectrometers. The ^{13}C NMR spectra were recorded on the Varian Model XL-100-12 FT NMR spectrometer at 25.2 MHz. The ^{1}H and ^{13}C NMR chemical shifts are presented in parts per million (δ) downfield from internal tetramethylsilane (Me_4Si) as deuteriochloroform ($CDCl_3$) solutions at ambient temperature (ca. 25–27 °C). Infrared spectra were recorded on a Beckman Model IR-4250 and Perkin-Elmer Model 257 spectrophotometers as films, mulls, or dilute solutions with polystyrene (1601.4 cm^{-1}) as an external reference.

Gas–liquid partition chromatography (GLC) analyses were performed on a Hewlett-Packard Model 5754B analytical instrument equipped with a flame-ionization detector (FID) and a GOW-MAC Model 550 gas chromatograph equipped with a thermal-conductivity detector. All GLC analyses were conducted on 10% and 15% DC-550 silicon oil on Chromosorb P (80–100 mesh) in stainless steel columns (12 ft × 0.125 in.).

Cumene, cyclohexene, α-phellandrene, α-terpinene, tetralin, and *d*-limonene are commercially available and were distilled from sodium metal under a nitrogen atmosphere. Dimethyl acetylenedicarboxylate was purchased from Aldrich Chemical Co. and used without further purification. Maleic anhydride was purchased from Fisher Scientific and required no further purification. Norbornene and norbornane are also commercially available.

CTH of Dimethyl Bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (5). General Procedure. A stirred neat mixture of the donor (4 mmol) and diester **5** (2 mmol) was treated with 10% palladium on carbon (50 wt/wt % based on diester **5**) in an 8-dram vial, and the suspension was heated at 110 °C. The reaction was quenched by cooling (ice bath, 0–5 °C) and a small aliquot removed for ^{1}H NMR analyses. The ^{1}H NMR results are summarized in Table III (see text).

Table III. CTH of Dimethylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate with 4-Substituted 1-Methylcyclohexenes



5 *endo*-**6**

donor	% CTH vs. time[a] 1 min	2 min	3 min	5 min	10 min
cyclohexene	11	16	17		
1-methylcyclohexene	79	87		94	96
1-methyl-4-isopropylcyclohexene	>99				
1-methyl-4-*tert*-butylcyclohexene	>99				

[a] Reaction conditions: 2.0 mmol of **5**; 4.0 mmol of donor with 50 wt/wt % of palladium based on **5**; 110 ± 2 °C. All measurements were made by using ^{1}H NMR spectroscopy.

CTH of *endo*-4. General Procedure. A mixture of the donor (1.10–1.20 mmol) and *endo*-**4** (2.0 mmol) was treated with 10% palladium on carbon (25% based on the weight of acceptor) and the suspension placed in an oil bath preheated to 110 °C. The stirred suspension was sampled at 1-min intervals for ^{1}H NMR analyses (see text for the results).

CTH of Diester 3 with Cyclohexene in Cumene Solution. Typical Procedure. A stirred suspension prepared from 10% palladium on carbon (122 mg, 1.1×10^{-4} mol of Pd), diester **3** (633 mg, 3.0 mmol), and cyclohexene (1.70 g, 21 mmol) in a 10-mL cumene solution was heated to reflux for 22 h under a nitrogen atmosphere. The suspension was cooled (ice bath), filtered, and concentrated (rotary evaporator) to an oil. ^{1}H NMR analyses indicated a mixture containing the products, diester **5** (88%) and *endo*-**6** (12%).

A similar run employing 10% palladium on carbon (41 mg, 3.9×10^{-4} mol of Pd), diester **3** (633 mg, 3.0 mmol), and cyclohexene (16.2 mg, 199 mmol) with cumene as the solvent gave a mixture of diester **5** (64%) and *endo*-**6** (36%) when the mixture was heated for 37 h.

Cyclopentadiene. Commercial bicyclopentadiene, in a fractional distillation apparatus, was immersed in an oil bath preheated to 185 °C. The monomer distilled at 38–40 °C (lit.[26] bp 40.5–41 °C) and was collected in a receiver cooled in an ice–water bath. The product was used immediately or stored at 0 °C.

***endo*-Dimethyl Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (*endo*-4).** Diester **4** was prepared by the method of Morgan et al.,[26] and its ^{1}H NMR spectrum is identical with the published spectrum.[27]

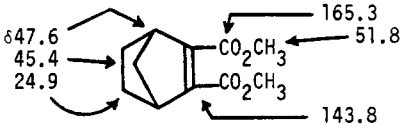
Dimethyl Bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (3). Cyclopentadiene (8.35 g, 0.13 mol) was added dropwise to cold (5 °C, ice bath) dimethyl acetylenedicarboxylate (15.6 g, 0.11 mol) with stirring. The resulting mixture was maintained at this temperature for 45 min. The solution was concentrated under reduced pressure (rotary evaporator) and then distilled under reduced pressure to give **3** (12.8 g, 56%) as a colorless oil which gradually turned a very pale yellow: bp 80–83 °C (0.05 mmHg) [lit.[28] bp 134–135 °C (10–11 mmHg)]; IR (neat) 1717 (s, C=O stretch, ester), 1627 and 1560 (s, C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.85 (t, 2 H, J = 2.0 Hz, C**H**=CH), 3.85 (t, 2 H, J = 2.0 Hz, CHC**H**$_2$C**H**), 3.75 (s, 6 H, CO_2CH_3), 2.21 and 2.07 (dd, 2 H, J = 7.4 Hz, CHC**H**$_2$CH).

Dimethyl Bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (5). A suspension of diester **3** (9.39 g, 0.045 mmol) and 10% palladium on carbon (500 mg) in 125 mL of acetone was stirred at atmos-

(26) Morgan, M. S.; Tipson, R. S.; Lowry, A.; Baldwin, W. E. *J. Am. Chem. Soc.* **1944**, *66*, 404.
(27) Kamezawa, N.; Sakashita, K.; Hayamizu, K. *Org. Magn. Reson.* **1969**, *1*, 405.
(28) Diels, O.; Alder, K. *Justus Leibigs Ann. Chem.* **1931**, *490*, 236.

pheric pressure under an atmosphere of hydrogen until 1.1 L had been consumed. GLC analysis of the reaction mixture revealed the presence of **5** along with a small amount of the completely reduced diester (endo-**6**). The suspension was filtered and concentrated (rotary evaporator), and the crude product (8.86 g) was distilled under reduced pressure, giving 7.85 g (84%) of a colorless oil, **5**: bp 118 °C (6–8 mmHg) [lit.[29] bp 132–133 °C (12 mmHg)]; ^{1}H NMR ($CDCl_3$) δ 3.77 (s, 6 H, CO_2CH_3), 3.30 (br s, 2 H, $CHCH_2CH$), 2.10–1.10 (m, 6 H, $CH_2CHCH_2CHCH_2$).

The ^{13}C NMR spectrum of diester **5** is shown below, and the assignments are consistent with the off-resonance coupling spectrum.



1,3-Cyclohexadiene (2). A neat solution of *trans*-1,2-dibromocyclohexane (61.9 g, 0.26 mol) was added dropwise to a mechanically stirred suspension of sodium hydroxide pellets (31.6 g, 0.79 mol) in 2-methoxyethanol (69.0 g, 1.13 mol) heated to ca 125 °C, allowing for the concurrent distillation of a water–crude product mixture. The distilling head temperature was maintained below 100 °C, and the distillation continued for 0.5 h after the addition was completed. The two components of the distillate were separated, and the organic layer was dried ($CaCl_2$) and distilled to afford **2**: 1.5 mL (44.6%); bp 79–80 °C (lit.[30] bp 78–88 °C); ^{1}H NMR ($CDCl_3$) δ 5.68 (s, 4 H, CH=CH), 2.05 (s, 4 H, ring CH_2).

1-Methylcyclohexene (12). 1-Methyl-1-hydroxycyclohexane (90.0 g, 0.81 mol) was prepared from the reaction of cyclohexanone (125 g, 1.27 mol) and methylmagnesium iodide [prepared from magnesium turnings (31.0 g, 1.29 mmol) and methyl iodide (183 g, 1.29 mol)]. The 1-methyl-1-hydroxycyclohexanone was added dropwise to a solution of concentrated phosphoric acid (35 mL), preheated to approximately 110–120 °C, allowing for the olefin–water mixture to distill into a cooled receiver (ice bath) at 5 °C. The crude product was decanted from water, dried ($MgSO_4$), and distilled over sodium to give 80 g (91%) of **12**, bp 105–107 °C (lit.[31] bp 108–109 °C). GLC analysis showed a product of 96% purity (the external olefin was the only other component).

1-Methyl-4-*tert*-butylcyclohexene (13). A solution of 4-*tert*-butylcyclohexanone (23.0 g, 0.149 mol) in anhydrous diethyl ether (100 mL) was added dropwise at 5 °C with stirring to methylmagnesium iodide, prepared by the addition of iodomethane (23.2 g, 0.164 mol) in dry ether (50 mL) to a suspension of magnesium turnings (3.93 g, 0.164 atom) in dry ether (50 mL). The suspension containing the ketone and Grignard reagent was heated (steam bath) for 2 h. The suspension was cooled to 5 °C (ice bath) and treated with 1.6 M hydrochloric acid (120 mL). The suspension was further heated as necessary to completely dissolve any unreacted magnesium. The solution was again cooled and the ethereal layer collected. The aqueous layer was extracted with ether (2 × 250 mL), and the ethereal layers were combined. The ethereal solution was treated with solid sodium bicarbonate until neutral, dried ($MgSO_4$), and concentrated (steam bath) to a dark yellow liquid which solidified upon standing. The solid was dissolved in a solution of benzene containing *p*-toluenesulfonic acid (1 g) and the mixture refluxed, allowing for the water to be collected in a Dean–Stark trap. After 2.6 mL of water had been collected, the mixture was cooled (ice bath), neutralized with solid sodium bicarbonate, dried ($CaCl_2$), and concentrated by distillation to give the crude product (15.9 g, 71%) in greater than 95% purity by GLC analysis. Distillation from sodium afforded the colorless product **13**: 11.0 g (49%); bp 77–78 °C (16 mmHg) [lit.[32] bp 53 °C (2.5 mmHg), greater than 99% purity by GLC analysis]; ^{1}H NMR ($CDCl_3$) δ 5.37 (s, 1 H, $CH=C(CH_3)$, 1.05–2.50 [m, 10H, $(CH_2)CHC(CH_3)$], 0.85 [s, 9 H, $-CH(CH_3)_3$].

1-Methyl-4-isopropylcyclohexene (14). A suspension of 10% platinum on carbon (0.40 g) in freshly distilled *d*-limonene (71.4 g, 0.524 mol) was treated with hydrogen gas at an initial pressure of 60 lb/sq in. The reaction was terminated after a pressure drop of 43.5 lb/sq in. had been recorded. The catalyst was removed by suction filtration, and colorless liquid distilled over sodium to afford 65 g (90%) of **14**, bp 77–77.5 °C (31 mmHg) [lit.[18] bp 77.5–78 °C (35 mmHg)].

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Registry No. 1, 110-83-8; 2, 592-57-4; 3, 947-57-9; *endo*-4, 39589-98-5; 5, 17931-56-5; *endo*-6, 4098-47-9; 7, 119-64-2; 8, 5989-27-5; 9, 4221-98-1; 10, 99-86-5; 12, 591-49-1; 13, 3419-74-7; 14, 5502-88-5; Pd, 7440-05-3; cyclopentadiene, 542-92-7; dimethyl acetylenedicarboxylate, 762-42-5; *trans*-1,2-dibromocyclohexane, 7429-37-0; 1-methyl-1-hydroxycyclohexane, 590-67-0; cyclohexanone, 108-94-1; methyl iodide, 74-88-4; 4-*tert*-butylcyclohexanone, 98-53-3; 4-*tert*-butyl-1-methylcyclohexanol, 6353-54-4.

(29) Diels, O.; Alder, K. *Justus Leibigs Ann. Chem.* **1931**, *490*, 240.
(30) Schaefer, J. P.; Endres, P. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 285.
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(32) Bordwell, F. G.; Landis, P. S.; Whitney, G. S. *J. Org. Chem.* **1965**, *30*, 3764.

Enones with Strained Double Bonds. 8. The Bicyclo[3.2.1]octane Systems[1]

Herbert O. House,* John L. Haack, William C. McDaniel, and Don VanDerveer

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

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The bicyclic enones bicyclo[3.2.1]oct-1-en-3-one (**4**) and 1-methylbicyclo[3.2.1]oct-5(6)-en-7-one (**5**) have been generated from various precursors and trapped by the addition of nucleophiles such as MeOH, PhSeH, or H_2O. The bridgehead enone **5** has also been trapped as its cycloadduct **31** with furan. Pyrolysis of this cycloadduct **31** reformed the bridgehead enone **5** that was trapped as the cycloadduct **32**. Related bridgehead enones **35** and **47** have also been generated as intermediates leading to products with bridgehead methoxy substituents.

Our earlier studies of enones with bridgehead double bonds have included the bicyclo[5.3.1]undecane **1**,[2] the bicyclo[4.3.1]decane **2**,[3] and the bicyclo[3.3.1]nonane **3**.[4] Since the variety and degree of reactivity observed for

0022-3263/83/1948-1643$01.50/0