dioxide, 71887-63-3; 3,3-dimethylthietane 1,1-dioxide, 27832-56-0; 3-methylthietane 1,1-dioxide, 25903-07-5; 3-*tert*-butylthietane 1,1-dioxide, 25903-05-3; 3-phenylthietane 1,1-dioxide, 25636-64-0; 3-(*p*-bromophenyl)thietane 1,1-dioxide, 71887-64-4; 3-methyl-3-phenylthietane 1,1-dioxide, 66809-99-2; 3,3-dimethylthietane, 13188-85-7; 3-methylthietane, 22438-40-0; 3-*tert*-butylthietane, 25903-02-0; 3-phenylthietane, 25636-63-9; 3-(*p*-bromophenyl)thietane, 55779-42-5; 3-methyl-3-phenylthietane, 66810-25-1; *p*-bromoacetophenone, 99-90-1; morpholine, 110-91-8; *p*-bromo-α-morpholinostyrene, 55779-43-6; 2-methyl-2-phenylpropane-1,3-diol, 24765-53-5; 2-phenylpropionaldehyde, 93-53-8; 2-methyl-2-phenylpropane-1,3-diol dibenzenesulfonate ester, 66810-41-1; norbornadiene, 121-46-0; 8-thiatetracyclo[2.2.1.1.0]octane 8,8-dioxide, 22061-75-2; **12**, 71927-86-1; **13**, 22061-74-1.

Correlation of Structure and Transannular Interactions in a Series of Cage Compounds

James C. Barborak,*[1a] Diana Khoury,[1b] Wilhelm F. Maier,[1c] Paul v. R. Schleyer,[1c] Edward C. Smith,[1a] William F. Smith, Jr.,[1a] and Christopher Wyrick[1a]

Departments of Chemistry, University of North Carolina at Greensboro, Greensboro, North Carolina 27412, and Princeton University, Princeton, New Jersey 08540, and the Institut für Organische Chemie, Universität Erlangen-Nürnberg, 8520 Erlangen, West Germany

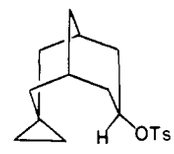
Received October 13, 1978

A series of cage systems with general structure **7** were synthesized. By variation of bridge C, the distance between functional groups A and B could be changed systematically and the chemical consequences of these changes investigated. Thus, Diels–Alder reactions between benzoquinone and cyclic dienes ranging from cyclobutadiene to cycloheptadiene, and including cyclooctatetraene, yielded endo dienes which were subsequently converted to cage structures photochemically. This transformation results in compounds **8**, **10**, **15**, **16**, and **17** with two transannular carbonyl groups positioned at varying distances. Under ketalization conditions some of these compounds—the ones with larger bridges C which brought the keto groups closer together—gave cyclized products rather than simple ketals. In the other cases, monoketals formed which were reduced to endo alcohols and studied further. Molecular mechanics calculations on hydrocarbon models for these systems provided a more quantitative basis for interpretation of the experimental results. The distance between A and B in **7** varied with the size of bridge C. The calculated energies of simulated ring-closure reactions (**40** → **39** and **41** → **39**) became more favorable as the number of atoms in bridge C was increased. These results parallel the experimental trends.

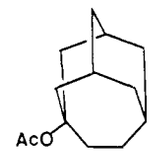
Rigid cage molecules are valuable substrates for the study of organic chemical transformations.[2] Compounds of this type have marked advantages over conformationally mobile molecules. Reaction centers in rigid molecules are fixed with respect to the remainder of the molecular skeleton; hence, perturbations due to conformational changes are effectively diminished or removed. This greatly simplifies the understanding of many chemical transformations and permits analysis of structure–reactivity relationships.

Not only mechanistic studies but also organic synthesis has taken advantage of the potential interaction between two reactive centers in conformationally restricted molecules. Polycyclic compounds of great rigidity and often of high symmetry, the so-called cage molecules, can result from transannular ring closure. For example, adamantanes and closely related compounds have been prepared from semirigid precursors. Thus, acetolysis of the spirocyclic tosylate **1** gives the homoadamantyl acetate **2**,[3] and 7-methylenebicyclo[3.3.1]nonan-3-one **3** provides the noradamantane **4** by reductive cyclization.[4] Transannular cyclizations of compounds such as **5** to produce the bridged structure **6**[5] are germane to the present work.

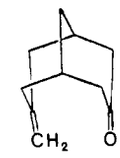
We wished to study the variations of chemical interactions in a series of closely related rigid molecules in which the transannular distance between functional groups could be altered systematically. The generalized pentacyclic system **7** fulfills these requirements. Compounds of this kind are readily available by sequences of Diels–Alder reactions and photochemical ring closures. The bridge C (in structure **7**) can be modified in order to alter the transannular relationship of functional groups A and B. Possibilities for such modifications and their consequences have been recognized previously.[6] Empirical force field



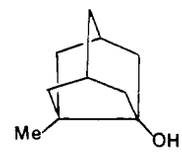
1



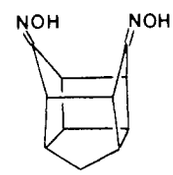
2



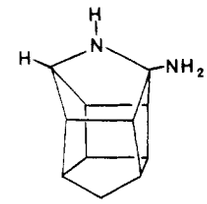
3



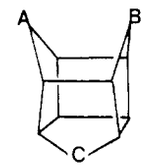
4



5



6



7

(1) (a) University of North Carolina at Greensboro. (b) Princeton University. (c) Universität Erlangen-Nürnberg.

(2) For reviews see: Bingham, R. C.; Schleyer, P. v. R. *Fortschr. Chem. Forschung.* **1971**, *18*, 1–102. McKervey, M. A. *Chem. Soc. Rev.* **1974**, *3*, 479–512. Fort, R. C., Jr. "Adamantane. The Chemistry of Diamond Molecules"; Marcel Dekker, Inc.: New York, 1976.

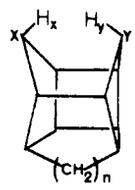
(3) Eakin, M. A.; Martin, J. C.; Parker, W. *Chem. Commun.* **1967**, 955–6.

(4) Eakin, M. A.; Martin, J. C.; Parker, W. *Chem. Commun.* **1965**, 206.

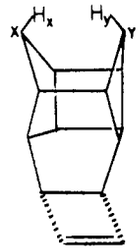
(5) Sasaki, T.; Eguchi, S.; Kiriyama, T.; Hiroaki, O. *Tetrahedron* **1974**, *30*, 2707–12.

0022-3263/79/1944-4761$01.00/0

Table I. Calculated Molecular Parameters for Various Cage Hydrocarbons



7a-d, n = 0-3



7e

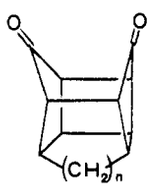
7f

compd		ΔH_f,[a] kcal/mol	strain, kcal/mol	C_x-C_y, Å	H_x-H_y, Å
7a, n = 0	A	64.82	92.44	2.790	2.396
	E	60.35	87.89	2.784	2.355
7b, n = 1	A	21.93	54.74	2.748	2.314
	E	19.62	52.59	2.751	2.254
7c, n = 2	A	15.69	53.69	2.691	2.227
	E	15.10	52.90	2.705	2.150
7d, n = 3	A	17.99	61.18	2.646	2.177
	E	16.93	59.86	2.669	2.082
7e	A	72.10	87.08	2.691	2.234
7f	A	73.51	88.49	2.688	2.233

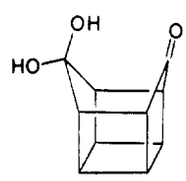
[a] Force fields employed: A, Allinger (1971); E, Engler-Andose-Schleyer.[7]

calculations[7] on hydrocarbon models **7a–7f** (see Table I) confirmed our strategy. Variations of the $(CH_2)_n$ bridge from n = 0 (**7a**) to n = 3 (**7d**) result in decreased separation between C_x and C_y or between H_x and H_y.

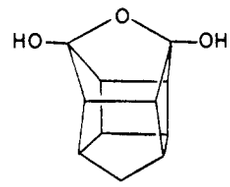
We were also encouraged in the choice of **7** by two pertinent experimental observations. Dione **8** forms the hydrate **9**, in which a single carbonyl group is involved,[8] whereas the related dione **10** gives the bridged hydrate **11**.[6,9] It seems reasonable that these products reflect



8 (n=0)
10(n=1)
15(n=2)
16(n=3)



9

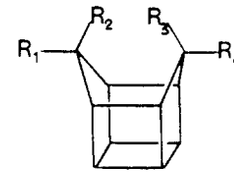


11

changes in the relative skeletal strain of the cage compounds due to the presence or the absence of the methylene bridge (C in **7**). By judicious selection of interacting groups A and B and methodical variation of C we hoped to be able to gain quantitative information about transannular interactions in such systems.

A second experimental observation shows that remote structural modifications can have a profound effect on the rates of rhodium(I) complex cleavages of strained polycyclic hydrocarbons closely related to those in which we were interested. The bishomocubane **12a** (R_1 = R_2 = H) is cleaved by bis[chloro(norbornadiene)rhodium(I)] to produce the diene complex **13** (R_1 = R_2 = H) with a second-order rate constant of 1.3×10^{-2} L mol^{-1} s^{-1} at 50 °C. An *endo*-methyl substituent on one of the methylene groups (**12b**, R_1 = H, R_2 = CH_3) causes diminution of the rate of ring opening by 1 order of magnitude, while two *endo*-methyl substituents (**12c**, R_1 = R_2 = CH_3) prevent

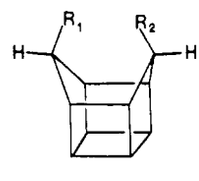
Table II. Calculated Molecular Parameters for Substituted Bishomocubanes



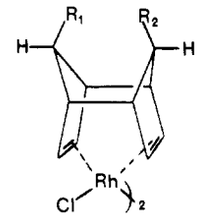
12a-f

compd		$\Delta H°_f$,[a] kcal/mol	strain, kcal/mol	Δ(strain),[b] kcal/mol
12a, R_1 = R_2 = R_3 = R_4 = H	A	64.82	92.44	
	E	60.35	87.89	
12b, R_1 = R_3 = R_4 = H; R_2 = CH_3	A	61.48	96.05	3.61
	E	56.14	90.76	2.87
12c, R_1 = R_4 = H; R_2 = R_3 = CH_3	A	59.72	101.24	8.80
	E	54.21	95.91	8.02
12d, R_2 = R_3 = R_4 = H; R_1 = CH_3	A	57.90	92.47	0.03
	E	52.98	87.60	-0.29
12e, R_1 = R_3 = H; R_2 = R_4 = CH_3	A	54.70	96.22	3.78
	E	49.10	90.80	2.91
12f, R_2 = R_3 = H; R_1 = R_4 = CH_3	A	50.98	92.50	0.06
	E	45.67	87.37	-0.52

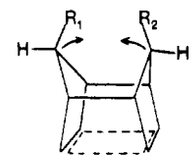
[a] Force fields employed: A, Allinger (1971); E, Engler-Andose-Schleyer.[7] [b] Increase in strain due to the substituent.



12a (R_1=R_2=H)
12b (R_1=H, R_2=CH_3)
12c (R_1=R_2=CH_3)



13



14

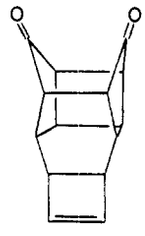
the reaction from occurring altogether.[10] This trend in reactivities has been reasonably attributed to steric compression involving the methyl groups during the course of ring opening. As the metal begins to insert itself into the carbon framework, distortion of the molecule necessarily results in pivoting about the four remaining bridgehead carbon atoms with concomitant increased crowding of R_1 and R_2. The overall effect is illustrated by **14**. The validity of this explanation was checked by force field calculations on **12a–12f** (Table II). *endo*-Methyl (**12b, 12e**) but not *exo*-methyl (**12d, 12f**) groups increase the total strain. The strain increase is most pronounced when two *endo*-methyl groups are present (**12c**).

Results

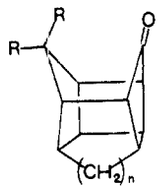
By the use of cyclobutadiene, cyclopentadiene, 1,3-cyclohexadiene, and 1,3-cycloheptadiene and subsequent photoisomerization[11] of the resulting tricyclic dienes, cage diones **8**, **10**, **15**, and **16** were prepared. A similar sequence

(6) Cookson, R. C.; Crundwell, E.; Hill, R. R.; Hudec, J. *J. Chem. Soc.* **1962**, 3062-75.
(7) Engler, E. M.; Andose, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005-25. Wertz, D. H.; Allinger, N. L. *Tetrahedron* **1974**, *30*, 1579-86. Sprague, J. T.; Allinger, N. L. *Ibid.* **1975**, *31*, 21-4. Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1-82.
(8) Barborak, J. C. Ph.D. Dissertation, University of Texas, 1968.
(9) This result appears to have been questioned more recently.[5] Our own work with dione **10** tends to confirm Cookson's results: Smith, E. C.; Barborak, J. C. *J. Org. Chem.* **1976**, *41*, 1433-7.
(10) Eaton, P. E.; Patterson, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 2573-5.
(11) For a review, see: Dilling, W. L. *Chem. Rev.* **1966**, *66*, 373-93.

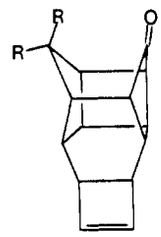
starting with cyclooctatetraene gave 17.[12] These molecules



17



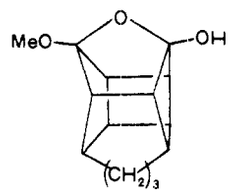
18 (R,R=-OCH$_2$CH$_2$O-, n=1)
19 (R,R=-OCH$_2$CH$_2$O-, n=2)
21 (R=R=OCH$_3$, n=0)
22 (R=R=OCH$_3$, n=1)
23 (R=R=OCH$_3$, n=2)
26 (R=R=OCH$_3$, n=3)



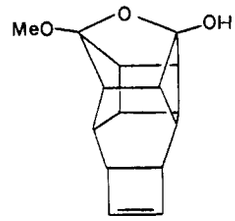
20 (R,R=-OCH$_2$CH$_2$O)
27 (R=R=OCH$_3$)

serve as starting materials for our experimental studies of the effect of modification of the remote bridge C in 7 on various reactions.

Ketalization was investigated first. Ethylene glycol in the presence of an acidic catalyst gave the expected monoethylene ketals 18, 19, and 20. In contrast, trimethyl orthoformate only reacted with diones 8, 10, and 15 in a straightforward manner to give the ketals 21, 22, and 23, respectively. Diones 16 and 17 gave mixed hydroxy ketals 24 and 25 rather than 26 or 27. Several attempts to obtain



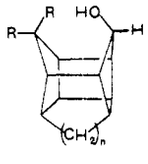
24



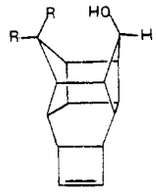
25

the normal monoketals 26 and 27 were unsuccessful. We attribute this difficulty to decreased strain in 24 and 25 in comparison with the open structures 26 and 27. This demonstrates the pronounced change in transannular behavior between functional groups A and B in 7 produced by modifications in group C.

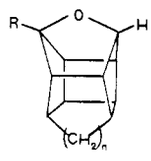
Reduction of the remaining carbonyl group of the monoethylene ketals 18, 19, and 20 and of the monodimethyl ketals 21, 22, and 23 with $LiAlH_4$ under the usual reaction conditions gave rise to the endo alcohols 28–33,



28 (R,R=-OCH$_2$CH$_2$O-, n=1)
29 (R,R=-OCH$_2$CH$_2$O-, n=2)
31 (R=R=OCH$_3$, n=0)
32 (R=R=OCH$_3$, n=1)
33 (R=R=OCH$_3$, n=2)



30 (R,R=-OCH$_2$CH$_2$O-)

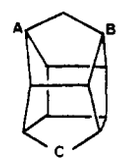


34 (R=-OCH$_2$CH$_2$OH, n=1)
35 (R=-OCH$_2$CH$_2$OH, n=2)
36 (R=-OCH$_3$, n=1)
37 (R=-OCH$_2$CH$_3$, n=1)
38 (R=-O(CH$_2$)$_3$CH$_3$, n=1)

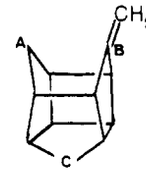
respectively. These alcohols were stable under neutral or basic conditions, as well as in the absence of solvent, but were rapidly converted to bridged ketals in the presence of traces of acid. Thus, 28 and 29 gave rise to the internal ketals 34 and 35, while 32 gave 36. Unfortunately, the rapidity of ketal–alcohol exchange in these compounds precluded rate measurements which would have provided

(12) Most of these compounds have been reported previously: 8, see ref 7 and 13; 10, see ref 6; 15, see ref 6; 16, this work; 17, see ref 6.

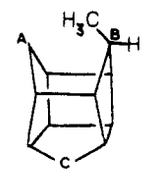
Table III. Calculated Molecular Parameters of Model Cage Compounds[a]



39



40



41

compd	ΔH_f, kcal/mol	strain, kcal/mol	Δ(strain), kcal/mol	r_{AB}, Å
39			41 - 39	
C = ---	76.55	94.06	-6.32	2.243
C = CH_2	30.80	53.90	-2.08	2.237
C = $(CH_2)_2$	20.12	48.80	4.68	2.222
C = $(CH_2)_3$	18.94	53.21	10.42	2.207
C = cyclobutyl	41.84	73.39	3.82	2.224
C = cyclobutenyl	75.86	79.11	4.11	2.235
40			40 - 39	
C = ---	88.39	87.45	-6.61	2.721
C = CH_2	44.90	49.54	-4.36	2.674
C = $(CH_2)_2$	37.62	47.84	-0.96	2.594
C = $(CH_2)_3$	39.14	54.94	1.73	2.542
C = cyclobutyl	59.12	72.21	-1.18	2.603
C = cyclobutenyl	93.23	78.03	-1.08	2.601
41			40 - 41	
C = ---	60.60	87.74	-0.29	2.903
C = CH_2	19.10	51.82	-2.28	2.818
C = $(CH_2)_2$	15.18	53.48	-5.64	2.757
C = $(CH_2)_3$	19.75	63.63	-9.69	2.710
C = cyclobutyl	36.04	77.21	-5.06	2.768
C = cyclobutenyl	70.35	83.22	-5.19	2.764

[a] Calculated with N. L. Allinger's MMI program (Program 318, QCPE, Indiana University, 1975) and Allinger's 1973 force field.[7]

quantitative data for comparison with the results of molecular mechanics calculations (Table I). These new ketals are quite stable. Alcohol exchange with 36, to produce the new ketals 37 and 38, only occurs slowly under reflux conditions with strong mineral acid catalysts.

Discussion

Force field calculations on the hydrocarbon model systems 39–41 (Table III) confirm the intuitively expected trend that as the size of the bridge C in 7 increases, the A–B distances decrease. Two hypothetical cyclization reactions, 40 → 39 and 41 → 39, model the processes studied. The Δ(strain) values for those processes (Table III, fourth column) best indicate the changes to be expected from variation in bridge C. Indeed, the process 40 → 39 is accompanied by decreasing strain release as n in C is varied from n = 0 to n = 2; when n = 3 an increase in strain is indicated. This is consistent with the observed chemical behavior of diones 8, 10, and 15 yielding the open ketals 21, 22, and 23, respectively, while only 26, with n = 3, provides the bridged ketal 24.

A similar trend, but a slightly different result is provided by comparison of 39 with 41 (a steric model of a ketone hydrate). The "crossover point", when 40 is more strained than 39, occurs when n = 2. The results indicate that n = 2 cases should have borderline behavior; small changes in structure or reaction conditions might change the relative stability of bridged or open structures. Such dual

behavior has been observed with dione **17**, which provided the open ketal **20** and the bridged ketal **25**. The force field calculations provide no explanation for the different behavior of diones **15** and **17**. Obviously the steric strain in the cage skeleton is not strongly influenced by the endocyclic cyclobutene ring, since the structures used to model **17** show almost the same strain and enthalpic values as do the $n = 2$ models.

Experimental Section

Nuclear magnetic resonance spectra were obtained with a Varian T-60 spectrometer and infrared spectra with a Perkin-Elmer Model 457 spectrophotometer. Melting and boiling points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc.

Pentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-7,10-dione (8). *endo*-Tricyclo[4.4.0.0^{2,5}]deca-3,8-diene-7,10-dione was prepared as described previously.[8,13] (Cyclobutadiene)iron tricarbonyl (12.8 g) was oxidatively degraded with ceric ammonium nitrate (160 g) in acetone solution at 0 °C in the presence of freshly sublimed *p*-benzoquinone (6.4 g). Degradation was conducted over a 1-h period. Workup involved pouring the reaction mixture into water, extracting with diethyl ether, washing the ether extracts with water, drying with $MgSO_4$, and evaporating the solvent to yield a dark oil which was subsequently purified by chromatography on silica gel (benzene) to produce 4.3 g (54%) of a yellow crystalline solid. Recrystallization from diethyl ether provided analytical material: mp 77–78 °C; NMR ($CDCl_3$) δ 3.7 (m, 2 H), 3.9 (m, 2 H), 6.2 (narrow m, 2 H), 6.8 (s, 2 H); IR ($CHCl_3$) 3040, 1677, 1550, 1294, 1258, 1120, 1039, 967, 935, 870 cm^{-1}.

The tricyclic diene (4.3 g) was dissolved in 200 mL of ethyl acetate and irradiated for 1.5 h with a 450-W medium-pressure lamp equipped with a Pyrex filter. The solvent was removed at reduced pressure to produce 4.78 g of an off-white crystalline solid. Recrystallization from anhydrous acetone at −20 °C yielded 2.5 g (61%) of the cage dione: mp 218–223 °C; NMR ($CDCl_3$) δ 3.3 (five-line m, 4 H), 3.7 (five-line m, 4 H); IR (hexachlorobutadiene) 2990, 1716, 1700, 1153, 1128, 1107, 1057, 655 cm^{-1}.

10,10-Dimethoxypentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-7-one (21). The cage dione **8** (2.5 g) and 1.82 g of trimethyl orthoformate were dissolved in 35 mL of dry methanol. After addition of a few milligrams of *p*-toluenesulfonic acid, the reaction mixture was stirred at ambient temperature for 18 h. Solvent was removed at reduced pressure to give 2.7 g of crude product, which was purified somewhat by washing with two 15-mL portions of cold diethyl ether to yield 1.85 g (45%) of the monoketal: NMR ($CDCl_3$) δ 3.2 (s, 3 H), 3.3 (s, 3 H), 3.5 (br, 8 H); IR ($CHCl_3$) 3000, 1735, 1325, 1145, 1105, 890 cm^{-1}.

***endo*-10,10-Dimethoxypentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-7-ol (31).** The monoketal **21** (0.9 g) was reduced with $LiAlH_4$ (0.17 g) in diethyl ether in the normal way to provide 0.54 g (59%) of a colorless oil which subsequently crystallized. Three recrystallizations from pentane at −30 °C produced analytical material: mp 27.5–29.5 ° C; NMR (CCl_4) δ 4.42 (d, 1 H), 3.50 (m, 1 H), 3.3 (6 H), 2.95 (narrow m, 8 H); IR (CCl_4) 3455, 2980, 1460, 1445, 1340, 1295, 1250, 1110, 1055, 1020, 940 cm^{-1}.

3-Methoxy-4-oxahexacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]undecane (Ring-Closure Product from 31). The dimethoxy alcohol **31** (0.15 g) was dissolved in methanol and a drop of aqueous HCl was added. The solution was allowed to stand at room temperature overnight, followed by removal of solvent at reduced pressure. The crystalline solid thus obtained was recrystallized twice from pentane at −78 °C to yield analytical material: mp 39–44 °C; NMR ($CDCl_3$) δ 5.1 (s, 1 H), 3.6 (s, 3 H), 3.3 (br, 8 H). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.54; H, 6.83.

Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (10). The Diels-Alder adduct was prepared by addition of cyclopentadiene (257 g, recently prepared) to 409 g of *p*-benzoquinone in 1.2 L of ethanol at a rate at which the exothermicity of the reaction was controlled. Cooling to room temperature and then to 0 °C to induce crystallization, followed by collection of the product by suction filtration and recrystallization from methanol (charcoal), yielded 495 g (74%) of the yellow crystalline adduct: mp 70–72 °C; NMR ($CDCl_3$) δ 6.4 (s, 2 H), 5.8 (s, 2 H), 3.3 (m, 2 H), 3.1 (m, 2 H), 1.3 (t, 2 H).

The Diels–Alder adduct (100 g) in 600 mL of ethyl acetate was irradiated for 2.5 h with a 450-W medium-pressure lamp equipped with a Pyrex filter, producing a white crystalline solid which partially separated from solution. At this point, NMR spectroscopy indicated the absence of olefinic absorptions. The solvent was evaporated and the residue was recrystallized from ethyl acetate (charcoal) to provide 79 g of the cage dione **10**: mp 245–246 °C; NMR (CCl_4) δ 3.3–2.6 (br, 8 H), 1.9 (AB pattern, 2 H); IR (CCl_4) 3000, 1765, 1220, 1195, 1120, 1065 cm^{-1}.

11,11-Dimethoxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one (22). The dione **10** (35 g) in 120 mL of anhydrous methanol was treated with 22.4 g of trimethyl orthoformate, 50 mg of *p*-toluenesulfonic acid was added, and the mixture was allowed to stand at room temperature for 20 h. The reaction mixture was poured into a mixture of 200 mL of 10% $NaHCO_3$ solution and 150 mL of CH_2Cl_2, and shaken, the layers were separated, and the organic solution was washed four times with 100-mL portions of water and then dried over anhydrous K_2CO_3. Evaporation of the solvent yielded a yellow oil which crystallized. Recrystallization from hexane provided 30 g (68%) of the monoketal **22**: mp 69–70 °C; NMR ($CDCl_3$) centered at δ 3.1 (2 sharp s, 6 H, 2 OCH_3, 3-Hz separation), δ 3.0–2.0 (br envelope, 8 H), centered at δ 1.55 (AB quartet, $J = 10$ Hz); IR ($CHCl_3$) 3000, 2845, 1740, 1460, 1335, 1115, 1070, 1020, 940, 905, 860 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.06; H, 7.54.

***endo*-11,11-Dimethoxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-ol (32).** The monoketal **22** (5 g) was reduced in the usual way with 0.43 g of $LiAlH_4$ in anhydrous ether at 0 °C. After the customary workup, evaporation of solvent provided a colorless oil which crystallized upon cooling (3.6 g, 72%). Recrystallization from pentane produced white crystals: mp 39–41 °C; NMR (CCl_4) δ 4.7 (d, 1 H, $J = 12$ Hz), 3.3 (singlet superimposed on a multiplet, 4 H), 3.1 (s, 3 H), 2.5 (br, 8 H), 1.4 (AB quartet, 2 H); IR (CCl_4) 3455, 2980, 2880, 1460, 1435, 1340, 1300, 1280, 1120, 1100, 1055, 1025, 1010, 970, 955 cm^{-1}.

3-Methoxy-4-oxahexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane (36). Dimethoxy alcohol **32** was allowed to stand in methanol solution (20 mL) with a trace of aqueous HCl for 24 h. Evaporation of methanol yielded 0.77 g (89%) of a colorless oil which was subsequently purified by vacuum distillation: bp 108 °C (0.75 mmHg); NMR ($CDCl_3$) δ 4.7 (br t, 1 H), 3.5 (s, 3 H), 2.7 (br, 8 H), 1.8 (AB quartet, 2 H); IR ($CHCl_3$) 2980, 2870, 2850, 1450, 1340, 1315, 1295, 1280, 1260, 1200, 1140, 1120, 1080, 1040, 1020, 980, 960, 910, 860 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.89; H, 7.28.

Pentacyclo[6.4.0.0^{2,7}.0^{3,11}.0^{6,10}]dodecane-9,12-dione (15). *p*-Benzoquinone (66 g) was stirred with 49 g of 1,3-cyclohexadiene in 150 mL of ethanol at 60 °C for 24 h. After the reaction mixture was cooled in an ice bath and the yellow crystalline product was collected by suction filtration, the product was recrystallized twice from ethanol to provide 54 g (55%) of the adduct: NMR ($CDCl_3$) δ 6.5 (s, 2 H), 6.1 (t, 2 H), 3.1 (br, 2 H), 2.9 (br s, 2 H), 1.4 (quartet, 4 H); IR (CCl_4) 3060, 2960, 2880, 1680, 1660, 1305, 1180, 1110, 1070, 890, 870, 835 cm^{-1}.

The Diels–Alder adduct (41 g) was dissolved in 500 mL of ethyl acetate and irradiated for 4 h with a 450-W lamp equipped with a Pyrex filter. The crystalline solid which separated was recrystallized from ethyl acetate (charcoal treatment) to give 8.1 g of the photoproduct: mp 251–254 °C; NMR ($CDCl_3$) δ 3.1 (br, 4 H), 2.6 (narrow m, 2 H), 2.2 (narrow m, 2 H), 1.8 (narrow m, 4 H); IR ($CHCl_3$) 2940, 2905, 1745, 1460, 1240, 1140, 1050, 830 cm^{-1}.

12,12-Dimethoxypentacyclo[6.4.0.0^{2,7}.0^{3,11}.0^{6,10}]dodecan-9-one (23). The cage dione **15** (7.85 g) was treated with 4.66 g of trimethyl orthoformate in 27 mL of methanol, to which a few milligrams of *p*-toluenesulfonic acid was added. After 24 h at room temperature, the reaction mixture was poured into dilute aqueous $NaHCO_3$ solution and extracted with methylene chloride. The extracts were washed with water, dried, and evaporated to provide 5 g of a yellowish oil, which was subsequently purified by chromatography on silica gel (hexane). The product obtained in this way was a colorless oil: NMR ($CDCl_3$) δ 3.2 (s, 6 H), 3.0–2.5 (br,

(13) Barborak, J. C.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 1328–9.

8 H), 1.7 (br s, 4 H); IR (CCl_4) 2970, 2950, 1755, 1465, 1335, 1320, 1240, 1195, 1185, 1145, 1115, 1080, 950, 920 cm^{-1}.

***endo*-12,12-Dimethoxypentacyclo[6.4.0.0^{2,7}.0^{3,11}.0^{6,10}]dodecan-9-ol (33).** The ketal **23** (1.43 g) was reduced with 0.23 g of $LiAlH_4$ in anhydrous ether, as before (see examples above). A colorless oil (1.20 g, 80%) was obtained, which crystallized. Recrystallization from pentane at −78 °C provided pure material: mp 56.6–57 °C; NMR ($CDCl_3$) δ 5.4 (d, 1 H), 3.3 (singlet superimposed on a multiplet, 4 H), 3.1 (s, 3 H), 2.5 (br, 8 H), 1.5 (d, 1 H); IR (CCl_4) 3440, 2960, 2870, 1290, 1175, 1145, 1105, 1065, 1045, 890 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.33; H, 8.53.

1-Methoxy-13-oxahexacyclo[6.4.1.0^{2,7}.0^{3,11}.0^{6,10}.0^{9,12}]tridecane (Ring Closure Product from 33). The dimethoxy alcohol **33** (0.3 g) was allowed to stand in 2 mL of methanol with a trace of aqueous HCl for 24 h. Evaporation of methanol provided 0.28 g of a colorless oil whose NMR spectrum agreed with the assigned structure, when compared with previously described examples (n = 0, 1): NMR ($CDCl_3$) δ 4.6 (t, 1 H), 3.4 (s, 3 H), 2.5–1.6 (br, 12 H).

Pentacyclo[7.4.0.0^{2,8}.0^{3,12}.0^{7,11}]tridecane-10,13-dione (16). 1,3-Cycloheptadiene was prepared from 1,3,5-cycloheptatriene by Na–NH_3 reduction after a method described in the literature.[14] Freshly sublimed *p*-benzoquinone (56 g) and 46.3 g of 1,3-cycloheptadiene in 300 mL of ethanol were heated at 50 °C for 2.5 weeks. After this period of time, NMR spectra indicated the absence of 1,3-cycloheptadiene. The reaction mixture was poured into water and extracted with ether, the ether layer was washed with water and dried with $MgSO_4$, and the solvent was evaporated at reduced pressure to yield 78 g of a black residue. Recrystallization from ethanol (charcoal treatment) provided 13.9 g of the Diels–Alder adduct (13%): mp 77–79 °C; NMR ($CDCl_3$) δ 6.75 (s, 2 H), 6.1 (m, 2 H), 3.2 (s, 2 H), 3.1 (m, 2 H), 1.7 (narrow m, 6 H); IR ($CHCl_3$) 3040, 2940, 2860, 1450, 1380, 1190 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.07; H, 6.78.

The Diels–Alder adduct described above was irradiated in 200 mL of ethyl acetate with a 450-W medium-pressure lamp equipped with a Pyrex filter; irradiation occupied 1.5 h. Solvent was removed at reduced pressure to provide 13 g of a yellowish solid; most of the color was removed by washing the solid with small amounts of cold diethyl ether to provide 7 g (50%) of white crystalline material. Recrystallization from ethanol yielded product: mp 160–162 °C; NMR ($CDCl_3$) δ 3.2 (m, 2 H), 3.0 (m, 2 H), 2.8 (m, 2 H), 2.1 (br envelope, 8 H); IR ($CHCl_3$) 2940, 2870, 1760, 1210, 1055 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.40; H, 7.00.

9-Methoxy-14-oxahexacyclo[7.4.1.0^{2,8}.0^{3,12}.0^{7,11}.0^{10,15}]tetradecan-1-ol (24). The dione **16** (0.08 g) was dissolved in 11 mL of anhydrous methanol containing 0.5 g of trimethyl orthoformate and 10 mg of *p*-toluenesulfonic acid. After 24 h the reaction mixture was poured into aqueous $NaHCO_3$ and extracted with ethyl ether. Drying of the ether layer with $MgSO_4$ and evaporation of solvent produced 0.6 g of a solid product, which was recrystallized from 30% ethyl ether–hexane to give white crystals: mp 80–83 °C; NMR ($CDCl_3$) δ 4.9 (br s, 1 H), 3.4 (s, 3 H), 2.7 (br s, 8 H), 1.6 (br s, 6 H); IR ($CHCl_3$) 3350, 2940, 1450, 1350, 1320, 1270, 1256, 1160, 920, 850, 830 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 72.09; H, 7.72.

Hexacyclo[8.4.0.0^{2,9}.0^{3,13}.0^{4,7}.0^{4,12}]tetradec-5-ene-11,14-dione (17). Freshly sublimed *p*-benzoquinone (19.2 g) and 19.4 g of cyclooctatetraene in 160 mL of *o*-dichlorobenzene was heated at 130 °C with stirring for 4 h. Solvent was removed at 80 °C and reduced pressure to give a black oily residue which crystallized. Recrystallization from ethanol provided 10 g (25%) of fine yellow crystals, mp 141–143 °C.

The Diels–Alder adduct (15 g) was irradiated in 200 mL of ethyl acetate with a 450-W medium-pressure lamp equipped with a Pyrex filter for 2 h. Removal of solvent at reduced pressure provided 15 g of a white crystalline solid, mp 194 °C (lit.[6] mp 195–196 °C). The material was used in the following reaction without purification: NMR ($CDCl_3$) δ 6.3 (s, 2 H), 3.0 (br, 6 H), 2.4 (br, 4 H); IR ($CHCl_3$) 2990, 2920, 1760, 1735 cm^{-1}.

10-Methoxy-15-oxaheptacyclo[8.4.1.0^{2,3}.0^{3,12}.0^{4,7}.0^{8,12}.0^{11,14}]pentadec-5-en-1-ol (25). The cage dione **17** described above (2.7 g) was placed in 20 mL of trimethyl orthoformate, 15 mg of *p*-toluenesulfonic acid was added, and the mixture was stirred at room temperature for 20 h. After this period, excess trimethyl orthoformate was removed at reduced pressure to yield 3.8 g of a yellowish solid, which was purified by recrystallization from ethyl acetate (charcoal treatment), producing a white crystalline solid: mp 198–200 °C; NMR ($CDCl_3$) δ 6.15 (s, 2 H), 4.5 (s, 1 H), 3.5 (s, 3 H), 2.5 (complex m, 10 H); IR ($CHCl_3$) 3350, 2980, 1350, 1310, 1140, 1070, 970, 910, 890, 850 cm^{-1}. Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 74.07; H, 6.69.

3-Ethoxy-4-oxahexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane (37). The ketal **36** (1.0 g) was dissolved in 30 mL of ethanol containing 0.6 g of 98% H_2SO_4, and the solution was refluxed for 24 h. The solution was poured into aqueous $NaHCO_3$ solution and extracted with benzene. After the solution was dried with $MgSO_4$, solvent was removed at reduced pressure to provide 0.96 g of a colorless oil, which was purified by double distillation: bp 105 °C (2 mmHg); NMR ($CDCl_3$) δ 4.6 (t, 1 H), 3.7 (q, 2 H), 2.5 (br, 8 H), 1.7 (AB quartet, 2 H), 1.3 (t, 3 H); IR ($CHCl_3$) 2990, 2880, 1380, 1340, 1295, 1280, 1150, 1120, 1020, 910, 870 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.48; H, 7.91.

3-(*n*-Butoxy)-4-oxahexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane (38). The 1-butanol exchange product was prepared in a manner exactly equivalent with that described for the corresponding ethoxy compound **37**, using 30 mL of 1-butanol containing 0.6 g of 98% H_2SO_4. Purification by distillation provided a colorless oil: bp 120 °C (2 mmHg); NMR ($CDCl_3$) δ 4.7 (t, 1 H), 3.6 (m, 2 H), 2.7 (br, 8 H), 1.5 (complex pattern made up of an AB quartet superimposed on a multiplet, 6 H), 0.9 (m, 3 H); IR ($CHCl_3$) 2970, 2880, 1460, 1340, 1280, 1160, 1080, 1010, 920, 870 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.62; H, 8.70.

Monoethylene Ketal of Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (18). The cage dione **10** (5.0 g), 1.9 g of ethylene glycol, and 15 mg of *p*-toluenesulfonic acid were dissolved in 50 mL of benzene, and the solution was heated at reflux while azeotroped water was collected with a Dean–Stark water separator. After cooling, the solution was washed once with 10% aqueous NaOH solution and then with water, the organic phase was dried over anhydrous K_2CO_3, and solvent was evaporated to produce a yellow oil which crystallized, 5.2 g (83%). The monoketal was recrystallized from hexane: mp 73–74 °C; NMR ($CDCl_3$) δ 3.9 (narrow m, 4 H), 3.1–2.4 (complex m, 8 H), 1.7 (AB quartet, 2 H). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.56; H, 6.63.

Monoethylene Ketal of *endo*-11-Hydroxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one (28). The $LiAlH_4$ reduction was conducted in the usual way, using 1.0 g of the keto-ketal **18** and a 1-molar excess of the reducing agent. Workup conditions were such that the reaction medium remained basic throughout,[17] and 0.9 g of a colorless oil which slowly crystallized was obtained. Purification involved chromatography on silica gel (elution with 10% ether–hexane), followed by recrystallization from diethyl ether at 78 °C: mp 61.5–63 °C; NMR ($CDCl_3$) δ 5.2 (d, 1 H), 3.95 (narrow m, 4 H), 3.6 (d of m, 1 H), 2.7–2.1 (br m, 8 H), 1.4 (AB quartet, 2 H); IR (CCl_4) 3481, 2970, 2870, 1450, 1350, 1300, 1280, 1120, 1017, 950, 935 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.78; H, 7.32. Found: C, 70.74; H, 7.37.

3-(2-Hydroethoxy)-4-oxahexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane (34). Allowing a sample of the endo alcohol **28** to stand for 17 h in methanol solution with a few drops of aqueous HCl led to complete conversion to the transannularly closed ketal **34**: NMR ($CDCl_3$) δ 4.7 (t, 1 H), 3.8 (s, 4 H), 3.3 (s, 1 H), 3.0–2.4 (m, 8 H), 1.8 (AB quartet, 2 H).

Monoethylene Ketal of *endo*-12-Hydroxypentacyclo[6.4.0.0^{2,7}.0^{3,11}.0^{6,10}]dodecan-9-one (29). The compound was prepared in a manner identical with that described above for the synthesis of **28**. Thus, the cage dione **15** (19.85 g), 7.4 g of ethylene

(14) Hafner, K.; Rellensmann, W. *Chem. Ber.* **1962**, *95*, 2567–78.

(15) This compound has been reported previously[16] but its physical constants are given erroneously and are actually those of the ring-closure product **34**.

(16) Eaton, P. E.; Cassar, L.; Hudson, R. A.; Hwang, D. R. *J. Org. Chem.* **1976**, *41*, 1445–8.

(17) Mićović, V. M.; Mihailović, M. L. J. *J. Org. Chem.* **1953**, *18*, 1190–1200. Cf.: Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1968; Vol. I, p 584.

glycol, and a catalytic amount of p-toluenesulfonic acid was refluxed in 130 mL of benzene for 16 h, while H_2O was removed with a Dean–Stark water separator. In this way, 23.4 g of crystalline solid was obtained, which was used without further purification: NMR ($CDCl_3$) δ 3.9 (br s, 4 H), 2.8 (broad unresolved multiplet, 4 H), 2.3 (broad unresolved multiplet, 4 H), 1.7 (poorly resolved AB pattern, 4 H).

The monoethylene ketal **19** (5.0 g) was reduced with 0.8 g of $LiAlH_4$ in diethyl ether, providing 4.2 g of a white crystalline solid, mp 76–78 °C. Recrystallization from hexane yielded an analytical sample: mp 76.5–77.5 °C; NMR (CCl_4) δ 5.35 (d, 1 H), 3.9 (symmetrical eight-line pattern, 4 H), 3.4 (d of m, 1 H), 2.7–1.3 (complex absorption, 12 H); IR (CCl_4) 3475, 2955, 1466, 1343, 1288, 1268, 1143, 1105, 1080, 1055, 1020, 953, 937, 923 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.96; H, 7.74.

Monoethylene Ketal of 6-Hydroxyhexacyclo[6.4.2.0^{2,7}.0^{4,14}.0^{5,13}.0^{9,12}]tetradec-10-en-3-one (30). The formation of the monoethylene ketal of the dione **17** and its subsequent reduction with $LiAlH_4$ in THF proceeded unexpectionally when methods outlined above for the synthesis of **28** and **29** were used. The endo alcohol **30** obtained in this way, after recrystallization from ethyl acetate, exhibited the following: mp 119–120.5 °C; NMR (CCl_4) δ 6.2 (s, 2 H), 5.4 (d, 1 H), 4.0 (complex m, 4 H), 3.4 (d of m, 1 H), 3.0–1.5 (complex, 10 H); IR (CCl_4) 3460, 3045, 2970, 2910, 1351, 1322, 1152, 1124, 1075, 1050, 1025 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.66; H, 7.06.

Acknowledgment. Financial support was provided at Greensboro by the Research Corporation and the Research Council of the University of North Carolina at Greensboro, at Princeton by the National Institutes of Health, and at Erlangen by the Fonds der Chemischen Industrie.

Registry No. 7a, 7172-92-1; **7b**, 4421-32-3; **7c**, 4421-33-4; **7d**, 69042-80-4; **7e**, 69028-00-8; **7f**, 69087-61-2; **8**, 31285-42-4; **10**, 2958-72-7; **12b**, 66819-91-8; **12c**, 66824-76-8; **12d**, 69087-57-6; **12e**, 69087-58-7; **12f**, 69087-59-8; **15**, 712-25-4; **16**, 69028-01-9; **17**, 71885-01-3; **18**, 58228-93-6; **19**, 62111-11-9; **21**, 66824-74-6; **22**, 69028-03-1; **23**, 69028-04-2; **24**, 69028-05-3; **25**, 69028-06-4; **28**, 58228-94-7; **29**, 69027-95-8; **30**, 71885-36-4; **31**, 69042-81-5; **32**, 69027-93-6; **33**, 69027-94-7; **34**, 69028-07-5; **36**, 71871-51-7; **37**, 69028-11-1; **38**, 69028-12-2; **39**, C = ---, 25107-14-6; **39**, C = CH_2, 704-02-9; **39**, C = $(CH_2)_2$, 71871-52-8; **39**, C = $(CH_2)_3$, 71871-53-9; **39**, C = cyclobutyl, 71871-54-0; **39**, C = cyclobutenyl, 71871-55-1; **40**, C = ---, 69027-97-0; **40**, C = CH_2, 71871-56-2; **40**, C = $(CH_2)_2$, 71871-57-3; **40**, C = $(CH_2)_3$, 71871-58-4; **40**, C = cyclobutyl, 71885-46-6; **40**, C = cyclobutenyl, 71885-45-5; **41**, C = CH_2, 71871-59-5; **41**, C = $(CH_2)_2$, 71871-60-8; **41**, C = $(CH_2)_3$, 71871-61-9; **41**, C = cyclobutyl, 71871-62-0; **41**, C = cyclobutenyl, 71871-63-1; 3-methoxy-4-oxahexacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]undecane, 69028-08-6; 1-methoxy-13-oxahexacyclo[6.4.1.0^{2,7}.0^{3,11}.0^{6,10}.0^{9,12}]tridecane, 69028-10-0; 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione, 51175-59-8; 1,4,4a,8a-tetrahydro-1,4-ethanonaphthalene-5,8-dione, 69685-89-8; 4a,9a-dihydro-5,9-ethenobenzocycloheptane-1,4-dione, 71885-00-2; 4a,10a-dihydro-5,10-etheno-6,8-benzocyclooctadiene-1,4-dione, 71871-64-2; *endo*-tricyclo[4.4.0.0^{2,5}]deca-3,8-diene-7,10-dione, 34231-42-0; cyclopentadiene, 542-92-7; p-benzoquinone, 106-51-4; 1,3-cyclohexadiene, 592-57-4; 1,3-cycloheptadiene, 4054-38-0; cyclooctatetraene, 629-20-9; ethanol, 64-17-5; 1-butanol, 71-36-3.

Para Substituent Carbon-13 Chemical Shifts in Substituted Benzenes. 1. Updating the σ^0_R Scale and Analysis of Aprotic Solvent Effects[1a]

John Bromilow,[1c] Robert T. C. Brownlee,*[1b] Vega O. Lopez,[1c] and Robert W. Taft*[1c]

Department of Chemistry, La Trobe University, Bundoora, 3083, Australia, and the Department of Chemistry, the University of California, Irvine, California 92717

Received November 20, 1978

The para carbon chemical shifts (C_p-SCS) for a selected series of monosubstituted benzenes have been measured in very dilute solutions of the nonpolar solvents cyclohexane and carbon tetrachloride and of the weakly polar solvent deuteriochloroform. These results provide the basis for the redefinition of σ^0_R values, which measure the ability of a substituent to delocalize π electrons to or from a neutral or unperturbed benzene ring. The new σ^0_R values are shown to make significant improvements in dual substituent parameter (DSP) correlations of appropriate data sets which are very sensitive to the effects of π electron delocalization. Applications include a definitive analysis of polar aprotic solvent induced C_p-SCS. These results offer strong support for both the new σ^0_R values and the basic assumptions of DSP analysis.

The σ^0_R scale is intended to be a quantitative measure of the ability of a substituent to delocalize π electrons into or from an unperturbed or "neutral" benzene ring.[2] The σ^0_R parameters have found wide application in dual substituent parameter (DSP) analysis[2d] and have been supported by the results of ab initio molecular orbital calculations.[2a] At the time the σ^0_R scale was developed, there were very few suitable substituent effect data for "neutral" systems. The scale was therefore heavily weighted by the ^{19}F NMR chemical shifts (F_p-SCS) of para-substituted fluorobenzenes.[2d] While F_p-SCS values are very sensitive to changes in π electron density (at or near F)[2c] and can be precisely measured at low concentrations in inert (nonpolar) solvents,[3] the F atom "probe" is a π electron donor which modifies the π electron donating or accepting ability of para substituents.[4]

With current FT instrumentation, the ^{13}C NMR chemical shifts of the para carbon atom (C_p-SCS) of monosubstituted benzenes can be obtained at high dilution in nonpolar solvents. The C_p-SCS values appear to be ideal for defining the σ^0_R scale since the ^{13}C "probe" is a part of the "neutral" benzene ring. Further, it is already known from measurements at higher concentrations[5] that C_p-SCS

(1) (a) This work was supported in part (UCI) by a grant from the U.S. Public Health Service. (b) La Trobe University. (c) University of California.

(2) (a) R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Am. Chem. Soc.*, **81**, 5352 (1959); (b) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960); (c) R. T. C. Brownlee and R. W. Taft, *J. Am. Chem. Soc.*, **90**, 6537 (1968); (d) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10**, 1 (1973); (e) W. J. Hehre, R. W. Taft, and R. D. Topsom, *ibid.*, **12**, 159 (1976); (f) R. D. Topsom, *ibid.*, **12**, 1 (1976); (g) W. F. Reynolds and R. A. McClellan, *Can. J. Chem.*, **55**, 536 (1977).

(3) R. T. C. Brownlee, S. K. Dayal, J. L. Lyle, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 7208 (1972).

(4) R. T. C. Brownlee, D. G. Cameron, R. D. Topsom, A. R. Katritzky, and A. F. Pozharsky, *J. Chem. Soc., Perkin Trans. 2*, 247 (1974).

0022-3263/79/1944-4766$01.00/0