organic solution was washed with water and dried. This solution was passed down a short column of silica gel (pentane elution) and 10 mg of **4** was recovered, $[\alpha]^{23}_D$ −5.3°, $[\alpha]^{23}_{436}$ −15.0° (*c* 0.8, dioxane). An increase in solvent polarity to 3% ethyl acetate in petroleum ether furnished 6 mg (30%) of epoxide **10**, $[\alpha]^{23}_D$ +4.2 (*c* 0.6, dioxane).

Chiral Epoxidation of 6. A 38-mg (0.24-mmol) sample of **6** was allowed to react with 35 mg (0.16 mmol) of crystalline monoperoxycamphoric acid exactly as described above. The recovered cyclooctatetraene (11 mg) proved to be optically inactive. The more polar epoxide **11** (12 mg, 43%) exhibited $[\alpha]^{23}_D$ +7.3° and $[\alpha]^{23}_{436}$ +19.4° (*c* 1.0, dioxane). This result proved consistent over several runs.

Acknowledgment. Financial support for this investigation was provided by the National Science Foundation.

Dynamic Properties of Chiral Cyclooctatetraenes. Total Inhibition of the Racemization Process by 1,4-Annulation

Leo A. Paquette* and Michael P. Trova[1]

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. *Received April 21, 1988*

Abstract: The chiral cyclooctatetraene **15** has been prepared in 10 steps from cycloheptene-1,2-dicarboxylic anhydride (**8**). Following Diels–Alder cycloaddition to isoprene, the anhydride functionality was transformed into a cyclobutene ring by Ramberg–Bäcklund ring contraction of the derived α-chloro sulfone. To introduce added unsaturation in the cyclohexene ring, it proved most expedient to isomerize the double bond in **13** first and to brominate **14** allylically as a prelude to dehydrobromination. The resulting triene underwent spontaneous isomerization to give (±)-**15**, which was resolved through formation and partial chromatographic separation of the diastereomeric urazoles **16** and **17**. The optically active [8]annulene did not experience racemization when heated extensively. The dynamic conformational potential of **15** has consequently been seriously inhibited by the 1,4-pentamethylene chain such that its homotopicity is maintained until thermal destruction.

In earlier work from this laboratory, a number of optically active cyclooctatetraenes were prepared, and the energetics of their ring inversion and bond shifting, both of which result in racemization, were quantified.[2] The combination of these and still earlier experiments[3,4] provide substantive credence to the proposition that mechanical tub-to-tub interconversion is mediated by planar alternate transition states typified by the parent D_{4h} structure **1**. This reaction mainfold is particularly well-accommodated by the kinetic consequences of varied 1,2-annulation.[5]

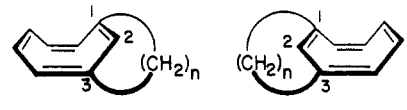
When the tool of proximal peripheral substitution is applied to evaluation of the actual pathway followed during π-bond alternation, the incremental increases in the free energies of activation can be interpreted as being compatible with the involvement of planar delocalized species related to **2**.[6] The energetic costs of bond shifting (BS) are usually higher than those associated with ring inversion (RI),[7] but are they high enough to be compatible with the antiaromatic character of **2**?[8] As a direct consequence of the associated potential energy surface, this pathway can be viewed as unattractive since the second-derivative matrix of force constants should have more negative eigenvalues than the single one required for a transition state (**3**) linking two equivalent nonplanar boat minima of the cyclooctatetraene.[9]

1 **2** **3**

The latter reasonable option involves a pseudorotation scheme where existing π bonds are simultaneously uncoupled with one set of neighboring carbons and formed with the other. Should this interconversion proceed along a path not bound by precise S_4 symmetry (for the parent system), then a transition state resembling **3** and not the crown conformation proposed by Dewar[10] would become a suitable descriptor.

In order to shed light on this delicate mechanistic distinction, additional studies of a highly refined nature become necessary. In pursuit of these objectives, we have set out to examine the dynamic behavior of three classes of annulated cyclooctatetraenes.

As concerns the enantiomeric 1,3-bridged systems **4**, racemization according to classical thinking will be dictated by the ease with which C_2-H can proceed into the interior of the polymethylene chain as planarization of the eight-membered ring occurs. With



4 **4'**

short chains, this pathway cannot, of course, be operative. On the other hand, pseudorotation does not demand planarization, and loss of optical activity can consequently be achieved without C_2 and its associated hydrogen ever entering the intraannular zone.[7b]

(1) Phillips Petroleum Fellow, 1986–1987.

(2) (a) Paquette, L. A.; Gardlik, J. M.; Photis, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 7096. (b) Gardlik, J. M.; Johnson, L. K.; Paquette, L. A.; Solheim, B. A.; Springer, J. P.; Clardy, J. *Ibid.* **1979**, *101*, 1615. (c) Gardlik, J. M.; Paquette, L. A.; Gleiter, R. *Ibid.* **1979**, *101*, 1617. (d) Paquette, L. A.; Gardlik, J. M. *Ibid.* **1980**, *102*, 5016. (e) Paquette, L. A.; Gardlik, J. M.; Johnson, L. K.; McCullough, K. J. *Ibid.* **1980**, *102*, 5026. (f) Paquette, L. A.; Hanzawa, Y.; McCullough, K. J.; Tagle, B.; Swenson, W.; Clardy, J. *Ibid.* **1981**, *103*, 2262. (g) Paquette, L. A.; Hanzawa, Y.; Hefferon, G. J.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 265. (h) Paquette, L. A.; Gardlik, J. M.; McCullough, K. J.; Hanzawa, Y. *J. Am. Chem. Soc.* **1983**, *105*, 7644. (i) Paquette, L. A.; Gardlik, J. M.; McCullough, K. J.; Samodral, R.; DeLucca, G.; Ouellette, R. *Ibid.* **1983**, *105*, 7649.

(3) (a) Anet, F. A. L. *J. Am. Chem. Soc.* **1962**, *84*, 671. (b) Anet, F. A. L.; Bourn, A. J. R.; Lin, Y. S. *Ibid.* **1961**, *86*, 3576. (c) Anet, F. A. L.; Bock, L. A. *Ibid.* **1968**, *90*, 7130.

(4) (a) Oth, J. F. M.; Merényi, R.; Martini, Th.; Schröder, G. *Tetrahedron Lett.* **1966**, 3087. (b) Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573. (c) Maier, G.; Sayrac, T.; Kalinowski, H.-O.; Askani, R. *Chem. Ber.* **1982**, *115*, 2214.

(5) Paquette, L. A.; Wang, T.-Z. *J. Am. Chem. Soc.* preceding paper.

(6) Paquette, L. A.; Gardlik, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 5033.

(7) (a) Paquette, L. A. *Pure Appl. Chem.* **1982**, *54*, 987. (b) For an exception to this trend, see: Paquette, L. W.; Wang, T.-Z. *J. Am. Chem. Soc.* **1988**, *110*, 3663.

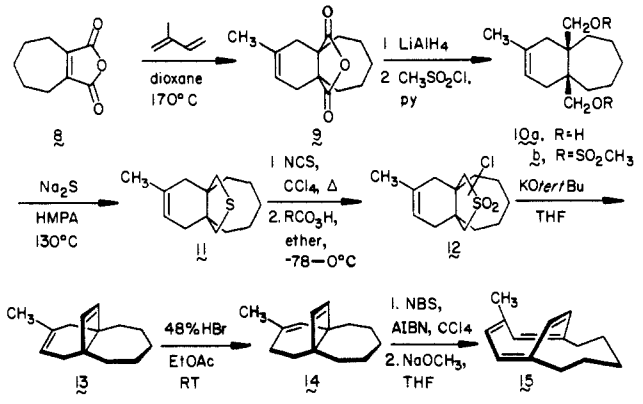
(8) (a) Allinger, N. L. *J. Org. Chem.* **1962**, *27*, 443. (b) Snyder, L. C. *J. Phys. Chem.* **1962**, *66*, 2299. (c) Finder, C. J.; Chung, D.; Allinger, N. L. *Tetrahedron Lett.* **1972**, *4677*. (d) Wipff, G.; Wahlgren, U.; Kochanski, E.; Lehn, J. M. *Chem. Phys. Lett.* **1971**, *11*, 350. (e) Allinger, N. L.; Sprague, J. T.; Finder, C. J. *Tetrahedron* **1973**, *29*, 2519.

(9) Ermer, O.; Klärner, F.-G.; Wette, M. *J. Am. Chem. Soc.* **1986**, *108*, 4908.

(10) Dewar, M. J. S.; Harget, A.; Haselbach, E. *J. Am. Chem. Soc.* **1969**, *91*, 7521.

0002-7863/88/1510-8197$01.50/0

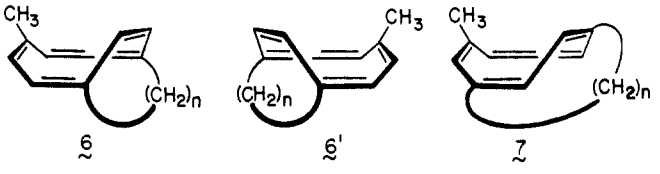
Scheme I



Additional valuable information might also be gained through examination of the response of 1,5-annulated systems such as **5** to thermal activation.[11] As with **4**, the longer polymethylene chains could permit conventional passage of the [8]annulene core through the loop,[12] but not otherwise. Should BS occur by

pseudorotation, racemization might not be seriously inhibited as the value of n is made relatively small. Consequently, kinetic measurements and correlation of activation parameters with existing k_{BS} and k_{RI} data in simpler cyclooctatetraenes should prove enormously revealing.

The 1,4-annulated cyclooctatetraenes **6** should offer interesting contrast to **4** and **5**, especially when constrained, e.g., when n = 5.[13] When bound by these limitations, bond shifting cannot be tolerated since **7** is a serious violator of Bredt's rule. Racemization



by ring inversion will also most certainly be rendered nonfunctional. The question may be posed whether an alternative mechanistic process will set in at more elevated temperatures and lead to net racemization.[14] Although **6** (**6'**) represents an extreme case of stringent architectural constraint on [8]annulene conformational mobility, the system represents a point of reference that is of key significance in the context of our projected examination of **4** and **5**.[16]

Herein we demonstrate that it is possible by 1,4-bridging to inhibit completely the ability of a chiral cyclooctatetraene to shed its optical activity.[17] Later papers shall deal with full details of the synthesis, resolution, and racemization behavior of **4** and **5**.[16]

Results and Discussion

Our strategy for arriving at **15** was based on synthesis of the [5.4.2]propellatriene, in expectation that this valence isomer would experience facile disrotatory opening of the 1,3-cyclohexadiene ring to afford the less strained bicyclic tetraene tautomer (Scheme I). In order to test the validity of this proposal, cycloheptene-1,2-dicarboxylic anhydride (**8**) was prepared from 2-carbethoxycyclooctanone[13a,18] and heated with isoprene in an autoclave at 170 °C. The adduct **9** could be conveniently isolated in 71% yield after recrystallization provided that dioxane was utilized as diluent and small amounts of hydroquinone were present to inhibit polymerization. Once dimesylate **10b** was reached, reaction with anhydrous sodium sulfide in hexamethylphosphoramide at 130 °C proceeded smoothly despite the 2-fold neopentyl character of the leaving-group centers to deliver sulfide **11** in 94% yield.

Heating **11** with 1 equiv of *N*-chlorosuccinimide in carbon tetrachloride solution produced a mixture of α-chloro sulfides, which were not purified but directly oxidized chemoselectively with monoperphthalic acid. Subsequent exposure of the isomeric α-chloro sulfones to potassium *tert*-butoxide in tetrahydrofuran at −78 °C induced Ramberg–Bäcklund ring contraction[19] and furnished **13** (61% after distillation). The ease with which cyclobutene ring formation occurs in this example is particularly noteworthy.

Rather unexpectedly, all attempts to introduce a second double bond into the six-membered ring of **13** uniformly met with failure. Although bromination with pyridinium perbromide appeared to prefer attack at the more strained olefinic center, this regioselectivity could be reversed with molecular bromine. However, all subsequent efforts to effect dehydrobromination[20] within this intermediate were to no avail. The allylic bromination of **13** was also intensively scrutinized. The sensitive mixture of allylic bromides produced with *N*-bromosuccinimide and AIBN could likewise not be induced to undergo appropriate 1,2- or 1,4-elimination.

This complication was obviated when it was recognized that **13** was capable of remarkably efficient (86%) isomerization to **14** when treated with 48% hydrobromic acid in ethyl acetate solution at room temperature. Once migration of the double bond had been achieved, it became possible to brominate the allylic ring methylene position regioselectivity and to effect the desired dehydrobromination with sodium methoxide in tetrahydrofuran.

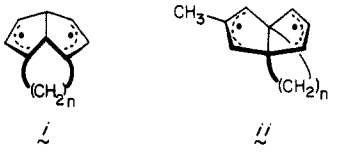
The ^1H and ^{13}C NMR spectra of **15** provide no hint as to the presence of the valence tautomer in equilibrium at 25 °C. Consequently, its concentration level under these conditions does not exceed 3% and is probably considerably lower. Nonetheless, when **15** is stirred with (−)-*endo*-bornyl-1,2,4-triazolinedione[21] in ethyl acetate solution at room temperature, the unobserved triene isomer can be captured with reasonable efficiency in the form of an equal mixture of **16** and **17**. Recrystallization of these urazoles from ethyl acetate/heptane provided quality crystals, X-ray analysis of which showed the unit cell to be composed of two molecules of each diastereomer.[22] Partial separation of **16** from

(11) The successful synthetic acquisition of this class of molecules has recently been announced: Paquette, L. A.; Trova, M. P. *Tetrahedron Lett.* **1987**, 2795; errata p 4354.

(12) For a recent example of "jump rope enantiomerization" involving 1,5-naphthalenophanes, see: Chang, M. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 4102.

(13) Further contraction in the value of n forces the cyclooctatetraene ring into the valence isomeric propellatriene structure having bicyclo[4.2.0]octatriene character: (a) Paquette, L. A.; Wingard, R. E., Jr.; Philips, J. C.; Thompson, G. L.; Read, L. K.; Clardy, J. *J. Am. Chem. Soc.* **1971**, *93*, 4508. (b) Paquette, L. A.; Philips, J. C.; Wingard, R. E., Jr. *Ibid.* **1971**, *93*, 4516.

(14) Transient bond formation to generate bicyclo[3.3.0]octadienediyl intermediates has been observed with *syn*-dibenzocyclooctatetraene derivatives.[15] While this pathway could not cause **6** to racemize, its operation in the series encompassed by **4** and **5** could lead to the formation of *achiral* diradicals i and ii. This issue will be discussed subsequently.[16]



(15) Salisbury, L. E. *J. Org. Chem.* **1978**, *43*, 4987, 4991.

(16) Paquette, L. A.; Luo, J.; Trova, M. P.; Wang, T.-Z., to be published.

(17) Preliminary communication: Paquette, L. A.; Trova, M. P. *Tetrahedron Lett.* **1986**, 1895.

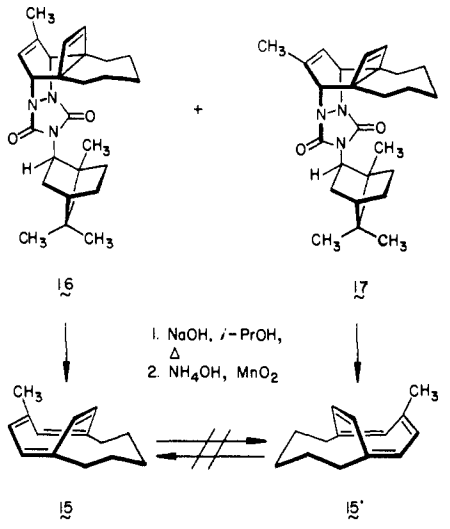
(18) Netherlands Patent Application No. 6,513,202, 1966; *Chem. Abstr.* **1966**, *65*, 20032*h*.

(19) Paquette, L. A. *Org. React. (N.Y.)* **1977**, *25*, 1.

(20) The conditions attempted included use of DBU, KO-*t*-Bu, Li_2CO_3/LiF, and Ph_3CLi in various solvents and at several temperatures.

(21) (a) Gardlik, J. M.; Paquette, L. A. *Tetrahedron Lett.* **1979**, 3597. (b) Paquette, L. A.; Doehner, R. F., Jr. *J. Org. Chem.* **1980**, *45*, 5105.

(22) Courtesy of Professor Robin Rogers (Northern Illinois University), whom we thank.



16 17

15 15'

17 was made possible by HPLC on a Waters Prep 500A instrument with peak shaving and recycling techniques. Diastereomeric excesses of 46% and 50%, respectively, were achieved as established by ^{1}H NMR analysis in $CDCl_3$ solution at 300 MHz. As has been observed in other contexts,[23] one methyl group in the chiral auxiliary is particularly sensitive to the diastereomeric environment. In this particular instance, its chemical shifts are located as sharp singlets at δ 0.79 and 0.78, sufficiently well resolved to allow independent integration.

With enriched samples of each urazole in hand, hydrolysis–oxidation was now effected. Whereas the less polar adduct, $[\alpha]^{22}_D$ −27.9°, gave **15** exhibiting $[\alpha]^{20}_D$ −33.7°, comparable treatment of the more polar urazole, $[\alpha]^{22}_D$ +14.1°, furnished the enantiomeric hydrocarbon, $[\alpha]^{20}_D$ +29.0°. Their 300-MHz ^{1}H NMR spectra were superimposable.

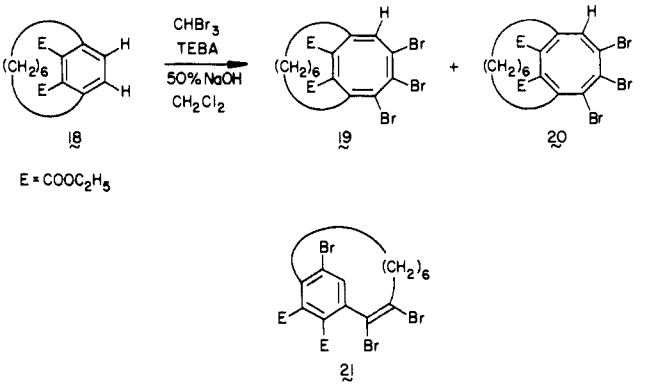
The first series of experiments executed with **15** involved heating a racemic sample dissolved in diglyme-d_{14} and sealed into a base-washed NMR tube in order to permit periodic spectral analysis. In a companion study, solutions of optically active **15** in diglyme were prepared and comparably heated for the purpose of monitoring any change in $[\alpha]_{365}$ with time. Both groups of samples were heated sequentially at 74.6 °C for 126 h, 83.2 °C for 36 h, and 94.6 °C for 24 h. Over this entire time span, no significant measurable spectral change in either sample was noted (Table I). Only when the temperature was increased to 158 °C and maintained for 22.7 h did a loss in optical activity (to the extent of ca. 7%) occur. However, this dropoff in $[\alpha]_{365}$ corresponded strictly to a comparable level of decomposition of the racemic cyclooctatetraene to unidentified byproducts.

These data establish that **15** constitutes the first example of a cyclooctatetraene that is incapable of either ring inversion or bond shifting. The preservation of the homochiral nature of its enantiomers until the onset of thermally induced destruction (perhaps by air oxidation) rules out the ability of the system to experience racemization by any pathway.

For the above reasons, consternation arose following completion of this work with the appearance of a report describing the reaction of **18** with excess dibromocarbene and claiming the isolation of **19** and **20** as byproducts.[24] Following correspondence with Professor Tochtermann[25] in which we questioned the validity of the structural assignment to **20** and urged more detailed examination of the molecule, the Kiel group succeeded in growing crystals of the trichloro analogue suitable for crystallographic analysis. This achievement, realized late in 1986, established the substance to actually be (*Z*)-1,2,14-tribromo-10,11-dicarbethoxy[8]paracyclophan-1-ene (**21**), the end product of a rather remarkable sequence of reactions. A molecule related to **7** and deemed by us to be incapable of isolation had not been produced after all![26]

Table I. Representative Optical Rotation Data Determined during Heating of Optically Active **15**

temp, °C	time, h	initial $[\alpha]^{22}_{365}$	$\Delta\alpha$	$\frac{\alpha_i - \alpha_f}{\alpha_i}$
74.55 ± 0.15	0	0.0667	0	0
	12.8	0.0647	0.002	2.9
	36.9	0.0647	0.002	2.9
	126.0	0.0647	0.002	2.9
83.15 ± 0.15	0	0.0067	0	0
	23.0	0.0657	0.001	1.5
	36.0	0.0643	0.0024	3.6
94.55 ± 0.15	0	0.0648	0	0
	24.0	0.0647	0.0001	0.1
106.05 ± 0.15	0	0.0647	0	0
	23.5	0.0637	0.001	1.5
158.0 ± 0.15	0	0.0640	0	0
	22.7	0.0595	0.0045	7.6



18 19 20

E = $COOC_2H_5$

21

In closing, it becomes important to emphasize that **15** is an extreme example of constrained belting. The question of whether less stringent architectural features might permit controlled racemization (and by which specific pathway) now must be addressed.

Experimental Section

9-Methyl-12,14-dioxo-13-oxa[5.4.3]propell-9-ene (9). A thick-walled glass tube was charged with **8**[13a,18] (2.49 g, 0.015 mol), isoprene (4.08 g, 0.06 mol), dry dioxane (20 mL), and hydroquinone (50 mg) and heated to 170 °C for 68 h. After cooling, the contents were evaporated in vacuo to leave a viscous oil that crystallized on standing. Recrystallization from hexane afforded cycloadduct **9** (2.49 g, 71%) as colorless needles: mp 70.5–71.5 °C; IR (CH_2Cl_2, cm^{-1}) 2930, 2860, 1870, 1750; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.59–5.57 (m, 1 H), 2.53–1.19 (m, 14 H), 1.71 (br s, 3 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 177.44, 177.15, 138.19, 120.98, 55.11, 54.57, 40.35, 36.34, 36.14, 35.88, 30.19, 26.43, 26.36, 22.64; MS, *m/z* (M^+) calcd 234.1256, obsd 234.1239.

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.78; H, 7.80.

***cis*-1,7-Bis(hydroxymethyl)-9-methylbicyclo[5.4.0]undec-9-ene (10a).** To a magnetically stirred, refluxing slurry of lithium aluminum hydride (0.63 g, 0.017 mol) in dry tetrahydrofuran (25 mL) was added a solution of **9** (1.06 g, 4.5 mmol) in the same solvent (5 mL). After being heated for 60 h, the reaction mixture was cooled and quenched with saturated sodium sulfate solution. The inorganic salts were removed by filtration, and the filtrate was evaporated in vacuo. The residue was recrystallized from hexane to give diol **10a** (0.92 g, 91%) as colorless plates: mp 130–131 °C; IR (CH_2Cl_2, cm^{-1}) 3400, 2920, 2860; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.25 (br s, 1 H), 3.75 (br, 2 H), 3.62–3.51 (m, 4 H), 2.04–1.38 (series of m, 17 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 131.11, 118.20, 68.25, 68.03, 42.44, 41.78, 38.67, 34.73, 34.42, 33.72, 27.49, 23.38, 22.06.

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.93; H, 10.84.

***cis*-1,7-Bis[[(methylsulfonyl)oxy]methyl]-9-methylbicyclo[5.4.0]undec-9-ene (10b).** To a cold (0 °C), magnetically stirred solution of **10a** (0.50 g, 2.3 mmol) in dry pyridine (10 mL) was added methanesulfonyl chloride (0.86 g, 7.5 mmol) dissolved in the same solvent (5 mL). After being

(23) Klobucar, W. D.; Paquette, L. A.; Blount, J. F. *J. Org. Chem.* **1981**, *46*, 4021.
(24) Königstein, V.; Tochtermann, W. *Tetrahedron Lett.* **1986**, 2961.
(25) Initiated on July 9, 1986.
(26) Königstein, V.; Tochtermann, W.; Peters, E.-V.; Peters, K.; von Schnering, H. G. *Tetrahedron Lett.* **1987**, 3483.

stirred for 2 h at 0 °C, the reaction mixture was poured onto cold 10% hydrochloric acid (170 mL). The resulting precipitate was removed by filtration and recrystallized from methanol to furnish **10b** as colorless irregular prisms (0.77 g, 91%): mp 86–87 °C dec; IR (CH_2Cl_2, cm^{-1}) 2920, 2880, 1360, 1180; ^1H NMR (300 MHz, $CDCl_3$) δ 5.28 (br s, 1 H), 4.27–4.07 (m, 4 H), 3.00 (br s, 6 H), 2.21–1.59 (series of m, 17 H); ^{13}C NMR (75 MHz, $CDCl_3$) 130.79, 117.71, 73.83, 41.56, 40.85, 37.12, 37.08, 37.04, 32.72, 32.62, 32.57, 26.88, 23.11, 21.78; MS, m/z ($C_{14}H_{20}^+$) calcd 188.1406, obsd 188.1580.

9-Methyl-13-thia[5.4.3]propell-9-ene (11). A slurry of sodium sulfide nonahydrate (300 g, 1.25 mol) in 1 L of freshly distilled hexamethylphosphoramide was distilled to remove water (bp below 60 °C/0.05 Torr) and cooled. Dimesylate **10b** (173.0 g, 0.455 mol) was added in one portion and the reaction mixture was heated to 130 °C for 20 h, cooled, and partitioned between water (1.5 L) and ether (1 L). The separated aqueous layer was extracted with ether (3 × 1 L), and the combined organic phases were washed with water (4 × 2 L) and brine (4 × 1 L), dried, and evaporated in vacuo. Following chromatography on silica gel (elution with petroleum ether), **11** (95.1 g, 94%) was obtained as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 5.21 (br s, 1 H), 2.72–2.64 (m, 4 H), 2.16–1.43 (series of m, 17 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 130.38, 117.60, 48.05, 47.23, 42.04, 39.06, 35.85, 35.68, 34.16, 27.16, 23.36, 22.02; MS, m/z (M^+) calcd 222.1442, obsd 222.1432.

For the purpose of characterization, a small portion of **11** was oxidized to the sulfone. To a cold (0 °C) solution of **11** (0.65 g, 2.9 mmol) in dry ether (25 mL) was introduced monoperphthalic acid (10.7 mL of a 0.55 M ethereal solution, 5.8 mmol) via a syringe. The reaction mixture was stirred at 0 °C for 1 h and at 25 °C for 2.5 h. The precipitate was removed by filtration and the filtrate was washed with 0.5 N sodium hydroxide solution (2 × 30 mL), water (1 × 30 mL), and brine (1 × 30 mL) prior to drying. Solvent evaporation afforded a solid, which was recrystallized from hexane to give colorless irregular prisms: mp 80.5–81.5 °C (0.73 g, 98%); IR (CH_2Cl_2, cm^{-1}) 2930, 2860, 1300, 1105; ^1H NMR (300 MHz, $CDCl_3$) δ 5.32 (br s, 1 H), 3.17–3.00 (m, 4 H), 2.23–1.53 (series of m, 17 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 130.32, 117.29, 62.61, 45.04, 44.15, 38.46, 35.97, 35.84, 33.67, 26.45, 23.07, 21.41; MS, m/z (M^+) calcd 254.1340, obsd 254.1358.

Anal. Calcd for $C_{14}H_{22}SO_2$: C, 66.10; H, 8.71. Found: C, 66.06; H, 8.67.

Chlorinative Oxidation of 11. A mixture of **11** (3.09 g, 0.014 mol), *N*-chlorosuccinimide (1.98 g, 0.015 mol) and dry carbon tetrachloride (100 mL) was heated at reflux for 1 h and cooled. The precipitate was removed by filtration and the filtrate was evaporated to leave a yellow oil. This oil was directly dissolved in dry ether (100 mL) and cooled to −78 °C. To this cold solution was added monoperphthalic acid (71 mL of 0.39 M ethereal solution, 0.028 mol) via a syringe over 2 h. The reaction mixture was allowed to warm slowly to room temperature whereupon the precipitate was removed by filtration. The filtrate was washed with 1 N sodium hydroxide solution (3 × 25 mL), water (3 × 25 mL), and brine (2 × 25 mL) prior to drying. Solvent evaporation afforded a mixture of the α-chloro sulfones **12**, which was recrystallized from hexane/dichloromethane to give colorless plates: mp 180–182 °C (1.79 g, 45%); IR (CH_2Cl_2, cm^{-1}) 2930, 2870, 1320, 1115; ^1H NMR (300 MHz, $CDCl_3$) δ 5.29 (br s, 1 H), 5.23 (s, 1 H), 3.25–2.85 (m, 2 H), 2.60–1.51 (series of m, 14 H), 1.67 (s, 3 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 130.46, 129.15, 117.34, 116.25, 80.00, 79.45, 78.25, 78.14, 77.21, 62.17, 47.91, 47.09, 42.71, 42.28, 41.51, 38.01, 37.36, 35.06, 33.75, 32.49, 32.33, 30.69, 26.20, 25.60, 24.62, 23.30, 22.81, 22.48, 21.28, 21.06; MS, m/z (M^+) calcd 288.0951, obsd 288.0923.

Anal. Calcd for $C_{14}H_{21}ClO_2S$: C, 58.22; H, 7.32. Found: C, 58.19; H, 7.41.

9-Methyl[5.4.2]propella-9,12-diene (13). To a cold (−78 °C) solution of **12** (0.55 g, 1.9 mmol) in dry tetrahydrofuran (25 mL) was added potassium *tert*-butoxide (0.69 g, 6.2 mmol) in one portion. After being allowed to warm slowly to room temperature, the reaction mixture was partitioned between water (50 mL) and pentane (35 mL). The aqueous phase was extracted with pentane (3 × 35 mL), and the combined organic phases were dried and concentrated. Distillation of the residue afforded diene **13** (0.22 g, 61%) as a colorless oil: bp 30–31 °C/0.03 Torr; IR (CH_2Cl_2, cm^{-1}) 3020, 2920, 2850; ^1H NMR (300 MHz, $CDCl_3$) δ 5.82 (d, J = 2.96 Hz, 1 H), 5.80 (d, J = 2.96 Hz, 1 H), 5.42 (br s, 1 H), 2.33–1.33 (series of m, 14 H), 1.72 (br s, 3 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 139.92, 139.21, 134.84, 119.75, 53.76, 52.99, 39.60, 36.86, 36.75, 33.91, 32.98, 25.71, 24.02; MS, m/z (M^+) calcd 188.1565, obsd 188.1561.

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.09; H, 10.76.

9-Methyl[5.4.2]propella-8,12-diene (14). A solution of **13** (30 mg, 0.16 mmol) in freshly distilled ethyl acetate (3 mL) was treated with two drops of 48% hydrobromic acid, stirred for 4 h, and poured into water (25 mL). The layers were separated, and the organic phase was washed with water (1 × 25 mL) and brine (2 × 25 mL), prior to drying and evaporation. The residue was chromatographed on silica gel (elution with petroleum ether) to give **14** as a colorless oil (26 mg, 86%): IR (CH_2Cl_2, cm^{-1}) 3030, 2920, 2850; ^1H NMR (300 MHz, $CDCl_3$) δ 6.00 (d, J = 2.73 Hz, 1 H), 5.76 (d, J = 2.73 Hz, 1 H), 5.16 (s, 1 H), 1.73 (s, 3 H), 1.91–1.34 (series of m, 14 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 138.63, 138.50, 137.03, 128.28, 53.41, 53.28, 37.25, 36.61, 32.65, 31.88, 27.60, 25.43, 24.92, 24.22; MS, m/z (M^+) calcd 188.1565, obsd 188.1567.

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.26; H, 10.66.

(±)-9-Methylbicyclo[5.4.2]trideca-7,9,11(1),12-tetraene (15). A mixture of **14** (43.6 mg, 0.232 mmol) and *N*-bromosuccinimide (41.4 mg, 0.233 mmol) in dry carbon tetrachloride (5 mL) containing AIBN (10 mg) was heated at reflux for 10 min. On cooling, succinimide was removed by filtration and the filtrate was concentrated in vacuo. To the residue dissolved in dry tetrahydrofuran (10 mL) was added excess sodium methoxide. The mixture was stirred at room temperature for 3 days and partitioned between water (5 mL) and petroleum ether (30 mL). The aqueous phase was extracted with petroleum ether (3 × 20 mL), and the combined organic layers were dried and evaporated prior to chromatography on silica gel (elution with petroleum ether). Cyclooctatetraene **15** was obtained as a colorless oil (0.012 g, 34% yield based on recovered **14**): ^1H NMR (300 MHz, $CDCl_3$) δ 5.86 (s, 2 H), 5.73 (s, 1 H), 5.62 (m, 1 H), 5.58 (s, 1 H), 2.38–2.30 (m, 2 H), 2.17–1.96 (m, 2 H), 1.93–1.82 (m, 2 H), 1.80 (s, 3 H), 1.49–1.16 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 142.70, 141.73, 140.27, 132.84, 132.79, 129.36, 127.50, 126.11, 37.54, 37.27, 31.18, 22.60, 18.69; MS, m/z (M^+) calcd 186.1409, obsd 186.1415.

Reaction of (±)-15 with (−)-*endo*-Bornyl-1,2,4-triazolinedione. Freshly prepared **15** (12 mg, 0.065 mmol) in freshly distilled ethyl acetate (2.5 mL) was stirred in the presence of (−)-*endo*-bornyltriazolinedione (20.2 mg, 0.0859 mmol) for 3 days. After removal of the solvent, the residue was chromatographed on silica gel (elution with 15% ethyl acetate in petroleum ether) to give a crystalline adduct as a 1:1 mixture of diastereomers **16** and **17** (15 mg, 56%): mp 192–193 °C; IR (CH_2Cl_2, cm^{-1}) 2930, 1720, 1700; ^1H NMR (300 MHz, $CDCl_3$) δ 5.91 (br s, 2 H), 5.72 (br s, 1 H), 4.33–4.31 (m, 1 H), 4.24–4.20 (m, 2 H), 2.40–1.10 (series of m, 17 H), 1.79 (br s, 3 H), 0.95 (s, 3 H), 0.87 (s, 3 H), 0.79 (s, 1.5 H, CH_3), 0.78 (s, 1.5 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 160.17, 160.01, 159.93, 159.88, 141.66, 139.76, 137.92, 137.77, 119.10, 118.99, 66.40, 61.75, 61.63, 59.03, 54.45, 54.39, 53.71, 51.62, 51.57, 47.69, 45.36, 32.54, 32.13, 32.02, 29.51, 29.44, 27.07, 26.50, 26.43, 26.28, 20.34, 20.24, 19.64, 18.74, 14.06, 14.03; $[\alpha]^{24}_D$ −4.6° (c 0.71, C_2H_5OH); MS, m/z (M^+) calcd 421.2729, obsd 421.2721.

Anal. Calcd for $C_{26}H_{35}N_3O_2$: C, 74.07; H, 8.37. Found: C, 73.73; H, 8.53.

Urazoles **16** and **17** were partially separated on silica gel (elution with 7% ethyl acetate in petroleum ether) with a Waters Prep 500A HPLC chromatograph operating in the recycle mode. The 1:1 mixture (0.850 g) dissolved in the minimum quantity of dichloromethane was injected onto the HPLC, and the leading and trailing edges were independently collected. The central portion of the peak was recycled two more times. The leading edge was determined by ^1H NMR to be enriched to the extent of 27/73: $[\alpha]^{22}_D$ −27.88°, $[\alpha]^{22}_{578}$ −29.52°, $[\alpha]^{22}_{546}$ −33.34°, $[\alpha]^{22}_{436}$ −57.25°, $[\alpha]^{22}_{365}$ −90.34° (c 0.94, C_2H_5OH). The trailing edge was a 75/25 diastereomeric mixture of **16** and **17**: $[\alpha]^{23}_D$ +14.12°, $[\alpha]^{23}_{578}$ +14.90°, $[\alpha]^{23}_{546}$ +17.22, $[\alpha]^{23}_{436}$ +33.03°, $[\alpha]^{23}_{365}$ +60.52° (c 0.77, C_2H_5OH).

Hydrolysis–Oxidation of 16/17. An equal mixture of urazoles **16** and **17** (14.4 mg, 0.034 mmol), sodium hydroxide (0.15 g), and dry isopropyl alcohol (1.5 mL) was heated at reflux for 36 h. On cooling, enough 10% hydrochloric acid was added to bring the solution to pH 2. To this solution were added concentrated ammonium hydroxide (to pH 9) and ether (10 mL). The resulting two-phase solution was treated with activated manganese dioxide (41.8 mg, 0.48 mmol) and stirred for 3 h. Inorganic salts were removed by filtration, and the separated aqueous phase was extracted with petroleum ether (3 × 10 mL). The combined organic layers were washed with brine (2 × 15 mL), dried, and evaporated. The residual oil was purified by chromatography on silica gel (elution with petroleum ether) to give 5.6 mg (88%) of (±)-**15**, identical in all respects with the material described above.

The optically active samples of **15** were prepared in entirely analogous fashion.

Attempted Racemization of Optically Active 15. A freshly prepared sample of (+)-**15** (10.4 mg) was placed in a base-washed 25-mL volumetric flask and diluted to the mark with freshly distilled diglyme. Approximately 1.1-mL-aliquot samples were placed into base-washed glass tubes (8 mm o.d., 6 mm i.d. × 20 cm). Each tube was subjected to three freeze–pump–thaw cycles and sealed under vacuum. The tubes

were placed in a constant-temperature oil bath, and the contents were allowed to equilibrate, and an accurate timer was started. Individual tubes were removed at various times and opened, and the contents placed in a polarimeter cell (1 dm). Optical rotations were measured at 365 nm. Some representative results are collected in Table I.

Thermal Stability Study of (±)-15. A freshly prepared sample of (±)-**15** (8 mg) was dissolved in diglyme-d_{14} (1 g) and placed in an NMR tube. The ^{1}H NMR spectrum was recorded and integrated with respect to internal protiated diglyme. The tube was placed in a constant-temperature oil bath (158.0 ± 0.15 °C) for 22.75 h. At the completion of the experiment, the ^{1}H NMR spectrum was again recorded and integrated. An approximate 7% decrease in the intensity of the olefinic proton absorption was noted. No characteristic new signals appeared in their stead.

Acknowledgment. The financial support of the National Science Foundation is gratefully acknowledged.

Registry No. 8, 10412-04-1; (±)-**9**, 106286-14-0; (±)-**10a**, 117021-90-6; (±)-**10b**, 117021-91-7; (±)-**11**, 106286-15-1; (±)-**11** (sulfone), 117021-92-8; (±)-**12**, 117021-93-9; (±)-**13**, 106286-16-2; (±)-**14**, 106286-17-3; (±)-**15**, 106313-33-1; (−)-**15**, 106286-19-5; (+)-**15**, 106313-32-0; **16**, 106286-18-4; **17**, 106357-98-6; isoprene, 78-79-5; (−)-*endo*-bornyl-1,2,4-triazolinedione, 117066-40-7.

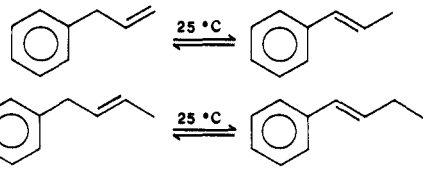
2-Indanone and Its Enol. The Effect of a Conjugated Phenyl Group on Enol and Enolate Stability

J. R. Keeffe,*,† A. J. Kresge,*,‡ and Y. Yin‡

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada. *Received May 9, 1988*

Abstract: Rate and equilibrium constants for the interconversion of 2-indanone with its enol and enolate ion have been determined in dilute aqueous acid and base solution (ionic strength = 0.10 M) at 25 °C. These measurements provide the keto–enol equilibrium constant, $pK_E = 3.84 \pm 0.04$; the acidity constant of the ketone ionizing as a carbon acid, $pK_a^K = 12.20 \pm 0.08$; and the acidity constant of the enol ionizing as an oxygen acid, $pK_a^E = 8.36 \pm 0.09$. Comparison of these results with values for acetone show that the effects of the benzene ring are large: a factor of $10^{4.4}$ on K_E, $10^{7.0}$ on K_a^K, and $10^{2.6}$ on K_a^E. Considerably smaller phenyl effects are estimated for the acyclic model ketone phenylacetone; reduced coplanarity in the latter is suggested as the major reason for the reduced effects. In terms of rate constants, the greater enol content of 2-indanone relative to acetone manifests itself in the acid-catalyzed reaction mainly as a largely reduced rate of enol ketonization and in the "uncatalyzed" reaction entirely by an increased rate of enolization. For hydroxide ion promoted enolate formation the phenyl effect appears roughly equally as an increase in the rate of enolate formation and a decrease in ketonization rate. It is suggested that the effects of a conjugated benzene ring on enol and enolate stability are fully expressed by the reactions of 2-indanone.

It is well established that replacement of a hydrogen atom or an alkyl group by phenyl stabilizes an attached carbon–carbon double bond. Hine's empirically based double bond stabilization parameters give $\Delta G = -4.9$ and -1.7 kcal/mol, respectively, for reactions 1 and 2.[1] Similarly, Benson's additivity parameters, also empirically based, give gas phase $\Delta G°_{298}$ values of -4.1 and -1.5 kcal/mol, respectively, for these two reactions.[2]



(1)

(2)

The influence of a conjugated phenyl group on double bond stabilization also has kinetic manifestations. Reactions 3 and 4, both examples of rate-controlling proton transfer to the double bond, give rate constant ratios k_{Ph}/k_{CH_3}, which are less than unity.[3,4] These results can be rationalized (in part) by invocation of superior initial-state stabilization by phenyl.[5]

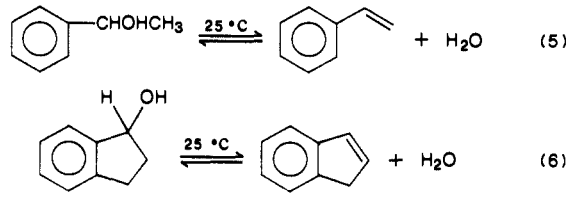
$$CH_2{=}C(R)CH_3 \xrightarrow{H^+} {}^{+}CH_3C(R)CH_3 \xrightarrow{H_2O} CH_3C(OH)(R)CH_3 \quad (3)$$

R = Ph, CH_3

$$CH_2{=}C(R)OC_2H_5 \xrightarrow{H^+} {}^{+}CH_3C(R)OC_2H_5 \xrightarrow{H_2O} CH_3C(O)R \quad (4)$$

R = Ph, CH_3

Incorporation of a double bond into a five-membered ring exalts this stabilizing effect of a conjugated phenyl group: for reactions 5 and 6, equilibrated in aqueous acid solution, $\Delta G = +2.19$ kcal/mol[6a] and -1.96 kcal/mol,[6b] respectively. The difference



(5)

(6)

† Present address: Department of Chemistry and Biochemistry, San Francisco State University, 1600 Holloway Avenue, San Francisco, California 94132.

‡ University of Toronto.

(1) Hine, J.; Flachskam, N. W. *J. Am. Chem. Soc.* **1973**, *95*, 1179–1185. Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Wiley: New York, 1975; pp 270–276.
(2) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968.
(3) (a) Oyama, K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1976**, *98*, 947–951. (b) Ciapetta, F. G.; Kilpatrick, M. L. *J. Am. Chem. Soc.* **1948**, *70*, 639–646.
(4) Kresge, A. J.; Sagatys, D. S.; Chen, H. L. *J. Am. Chem. Soc.* **1977**, *99*, 7228–7233.
(5) Chiang, Y.; Chwang, W. K.; Kresge, A. J.; Robinson, L. H.; Sagatys, D. S.; Young, C. I. *Can. J. Chem.* **1978**, *56*, 456–460.
(6) (a) Schubert, W. M.; Lamm, B. *J. Am. Chem. Soc.* **1966**, *88*, 120–124. (b) Keeffe, J. R.; Fleischman, M. F., unpublised results. Flesichman, M. F. M.S. Thesis, San Francisco State University, 1969.

0002-7863/88/1510-8201$01.50/0