reactant concentration at the micellar surface. The relatively small difference between the second-order rate constants in water and in the functional micelles may be due to a relief of the Coulombic repulsions between the carbocation and the micellar cationic head groups in the transition state.

We have no estimate of the molar volume element of reaction in clusters of **2**, but k_M in these clusters is not much smaller than in micelles of **1** (Table II), despite differences in the solvents, so that the factors which control reactivity in micelles are at work in these hydrophobic clusters. Transition-state stabilization, or activation of the anionic nucleophile by cationic micelles or hydrophobic clusters, seems to be relatively unimportant, as compared with the concentration effect, as is general for micellar rate enhancements.[21] The overall reaction of MG$^+$ with **2** is faster than that with choline in H_2O by a factor of almost 10 (Figure 1 and ref 6), and the difference would probably have been greater if reaction with **2** could have been followed in H_2O instead of in H_2O/MeCN. Addition of an organic solvent slows reactions assisted by hydrophobic tri-*n*-octylalkylammonium ions, probably by reducing substrate binding to the clusters.[11]

The pseudophase model readily accommodates chemical reactivity in micelles and many of the physical properties of aqueous micelles, and it can be applied to reactions in solutions of hydrophobic ammonium ions and to reactions in a variety of "organized assemblies".[24,25]

Acknowledgment. Support of this work by the National Science Foundation (Organic Chemical Dynamics Program) is gratefully acknowledged.

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(21) Transition-state effects are important for unimolecular reactions in micelles[22] and in some aromatic substitutions.[23]

(22) Bunton, C. A.; Fendler, E. J.; Sepulveda, L.; Yang, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 5512. Al-Lohedan, H.; Bunton, C. A.; Mhala, M. *Ibid.* **1982**, *104*, 6654.

(23) Bunton, C. A.; Moffatt, J. R.; Rodenas, E. *J. Am. Chem. Soc.* **1982**, *104*, 2653.

(24) Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley-Interscience: New York, 1982.

(25) Kinetic evidence which appears at first sight to be inconsistent with the pseudophase model is discussed in ref 26.

(26) Bunton, C. A.; Savelli, G.; Romsted, L. S. *J. Am. Chem. Soc.* **1979**, *101*, 1253. Nome, F.; Rubira, A. F.; Franco, C.; Ionescu, L. G. *J. Phys. Chem.* **1982**, *86*, 1881. Broxton, T. J. *Aust. J. Chem.* **1981**, *34*, 2313.

Stereochemistry of the Reaction of 7-Substituted Norbornadienes with Iron Carbonyls. 3. Reaction of Fe(CO)$_5$ with 7-(Benzoyloxy)norbornadiene

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Thermal reaction of 7-(benzoyloxy)norbornadiene with iron pentacarbonyl affords a cage dimer, 7,12-bis(benzoyloxy)heptacyclo$[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]$tetradecane (**1**, 29%), an anti,exo,trans,endo,anti (AXTNA) dimer ketone (**2**, 1%), a syn,endo,trans,endo,syn (SNTNS) dimer ketone (**3**, 2%), an anti,exo,trans,exo,anti (AXTXA) dimer ketone (**4**, 3%), and a novel cage dimer ketone (**5**, 0.4%). The structures of **2** and **3** were established via single-crystal X-ray structural analysis. The structures of **4** and **5** were gleaned via analysis of the proton and carbon-13 NMR spectra of these compounds. Thermal reaction of 7-[(*p*-methoxybenzoyl)oxy]norbornadiene (**6**) with Fe(CO)$_5$ afforded the corresponding cage dimer (**7**, 23%) and an anti,exo,trans,exo,anti (AXTXA) dimer ketone (**8**, 4%). The regiospecificity that has been noted previously in the case of Fe(CO)$_5$-promoted coupling of 7-*tert*-butoxynorbornadiene to carbon monoxide clearly is not a feature of the corresponding reactions reported herein.

As part of a continuing program that is involved with the study of the stereochemistry and mechanism of thermal reactions of iron pentacarbonyl with 7-substituted norbornadienes,[1-3] we have recently examined the reaction of Fe(CO)$_5$ with 7-(benzoyloxy)norbornadiene. In earlier work, we have exploited the Fe(CO)$_5$-promoted cyclodimerization of 7-substituted norbornadienes for the purpose of synthesizing novel, substituted heptacyclo$[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]$tetradecanes.[4-6] In addition, we have shown that the presence of a 7-Lewis base substituent in norbornadiene dramatically affects the stereochemical outcome of its Fe(CO)$_5$-promoted coupling to carbon monoxide.[2,3] The present study was undertaken in an effort to further delineate the role of the syn-7-Lewis base substituent in directing the course of this interesting coupling reaction.

In general, Fe(CO)$_5$-promoted coupling of 7-substituted norbornadienes to carbon monoxide is a highly stereospecific and regiospecific process. In the case of 7-*tert*-butoxynorbornadiene, while several products are formed

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(1) Speert, A.; Gelan, J.; Anteunis, M.; Marchand, A. P.; Laszlo, P. *Tetrahedron Lett.* **1973**, 2271.

(2) Marchand, A. P.; Hayes, B. R. *Tetrahedron Lett.* **1977**, 1027.

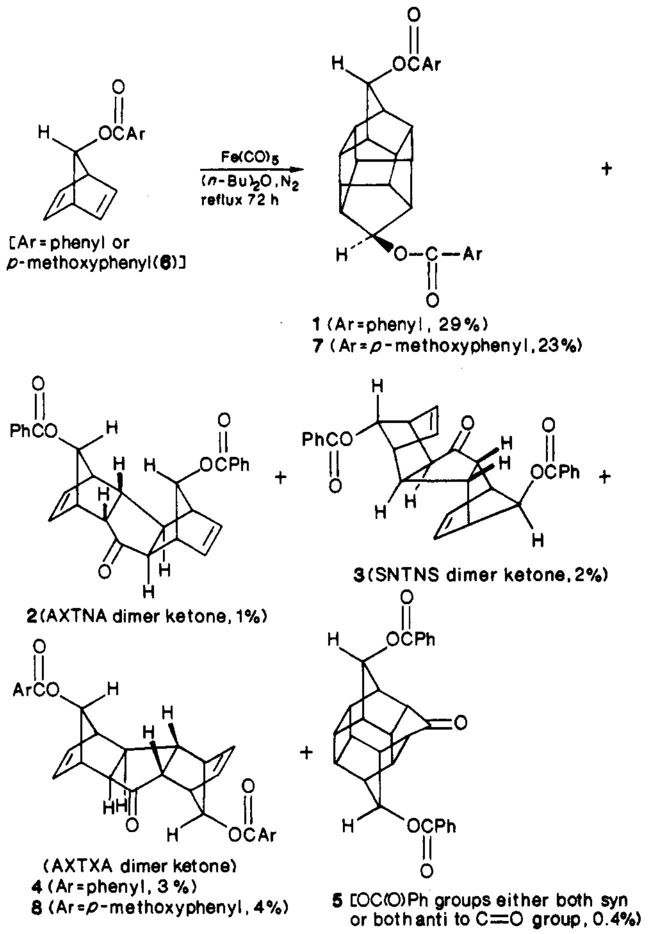
(3) Marchand, A. P.; Goodin, D. B.; Hossain, M. B.; van der Helm, D. *J. Org. Chem.* **1984**, *49*, 2897.

(4) Marchand, A. P.; Earlywine, A. D. *J. Org. Chem.* **1984**, *49*, 1660.

(5) Marchand, A. P.; Wu, A.-H. *J. Org. Chem.* **1985**, *50*, 396.

(6) Neely, S. C.; van der Helm, D.; Marchand, A. P.; Hayes, B. R. *Acta Crystallogr., Sect. B* **1976**, *B32*, 561.

Scheme I



in its thermal reaction with $Fe(CO)_5$, only *one* of 36 possible dimer ketones[7] and only *one* of 2304 possible linear trimer diketones[8] are formed.[2] In contrast to this result, we now report that the corresponding reaction of $Fe(CO)_5$ with 7-(benzoyloxy)norbornadiene produces *several* dimer ketones (vide infra). Hence, the unusual regiospecificity that has been noted in earlier examples[1-3,9a,b] clearly is not a feature of the present reaction.

The products of the reaction of $Fe(CO)_5$ with 7-(benzoyloxy)norbornadiene are shown in Scheme I. The structures of two of the dimer ketones, i.e., the anti,exo,trans,endo,anti isomer (AXTNA, **2**) and the syn,endo,trans,endo,syn isomer (SNTNS, **3**), were established via single-crystal X-ray crystallographic analysis. Experimental crystallographic data for **2** and **3** are presented in Table I.

Compound **3** possesses a twofold axis coincident with the ketone linkage in the central cyclopentanone ring. Both halves of this molecule are equivalent within 1σ. The cyclopentanone ring and the ketone oxygen atom are essentially coplanar in **2** and in **3**; the slight deviations from planarity are toward a "half-chair" conformation. The carbon–carbon bonds that are directly attached to the cyclopentanone rings in **2** and **3**, respectively, display lengthening that is now recognized as being characteristic of systems of this type.[3,7,8] The geometries of **2** and of **3** indicate the presence of considerable strain in these molecules; bond angles deviate significantly from idealized values, and torsion angles indicate an eclipsed rather than staggered arrangement of C–C and C–H bonds.

Table I. Experimental Crystallographic Data

	2(AXTNA)	3(SNTNS)
formula	$O_5C_{29}H_{24}$	$O_5C_{29}H_{24}$
M_r, amu	452.51	452.51
crystal dimensions, mm	0.20 × 0.38 × 0.48	0.15 × 0.48 × 0.60
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
cell dimensions,[a]		
a, Å	9.221 (2)	6.577 (2)
b, Å	9.972 (2)	8.751 (2)
c, Å	13.063 (2)	21.738 (6)
α, deg	94.28 (2)	78.22 (2)
β, deg	105.33 (1)	81.26 (3)
γ, deg	99.83 (2)	69.88 (3)
V, Å^3	1132 (6)	1131 (14)
Z	2	2
density (calcd), g·cm^{-3}	1.327	1.328
scan method	$\theta/2\theta$	$\theta/2\theta$
radiation	Cu Kα (λ = 1.54180 Å) Ni filtered	Mo Kα (λ = 71069 Å) graphite monochromator
temperature	ambient	ambient
2θ range, deg	2–150	3–50
max scan time, s	45	45
scan angle, deg	0.90 + 0.20 tan θ	1.0 + 0.20 tan θ
monitor reflections	3 orientation checks every 200 reflections 3 intensity checks every 2 h	
variation in monitors, %	2	2
total data	4793	4084
unique data	4668	3965
observed data, $I_0 \geq 2\sigma(I)$	3762	2165
μ, cm^{-1}	6.47 (Cu Kα)	0.52 (Mo Kα)
$F000$	476	476
R, R_w	0.049, 0.067	0.067, 0.064
w	σ_F^{-2}	σ_F^{-2}

[a] Lattice constants calculated from 25 high angle reflections.

The structure of the corresponding anti,exo,trans,exo,anti (AXTXA) dimer ketone (**4**) could be gleaned via examination of its proton NMR spectrum. Key features in this regard are (i) the sharp AB pattern centered at δ 2.5 that corresponds to the cyclopentanone ring protons and establishes the trans relationship between the β and β′ cyclopentanone C–H bonds (for which J_{HH} = 0 Hz) and (ii) the existence of stereospecific long-range coupling, $^4J_{HH}$,[11] between the vinyl protons (δ 6.21) and the bridge proton, C*H*OC(O)Ph (δ 4.86). The existence of this long-range coupling, revealed via nuclear magnetic double resonance experiments, confirms that the bridge 7-benzoyloxy substituents occupy the anti bridge position in dimer ktone **4**.

In addition, a fourth dimer ketone was obtained from this reaction in very low yield (0.4%). This product is unusual; its mass spectrum indicates it to be isomeric with **2–4**, yet its ^1H and ^{13}C NMR spectra indicate the absence of any C=C unsaturation. In addition, the ^{13}C NMR spectrum of this compound displays only 13 signals; hence, it must contain a twofold symmetry element (i.e., a mirror plane and/or a C_2 axis). We were unable to obtain a single crystal of this material of sufficient quality to permit direct determination of its structure via single-crystal X-ray structural analysis. On the basis of the spectral information noted above, we tentatively assign the novel cage structure **5** (Scheme I) to this dimer ketone.

There is considerable evidence that suggests that norbornenes and norbornadienes bearing 7-oxygen-containing

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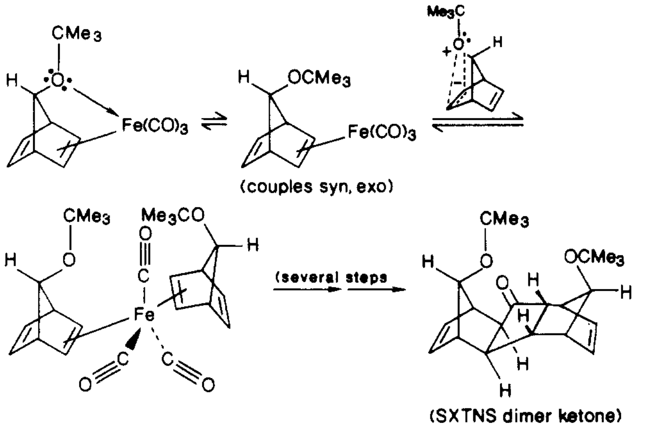
[7] Ealick, S. E.; van der Helm, D. *Cryst. Struct. Commun.* **1975**, *4*, 369.

[8] Ealick, S. E.; van der Helm, D.; Hayes, B. R.; Marchand, A. P. *Acta Crystallogr. Sect. B* **1978**, *B34*, 3219.

Scheme II



substituents undergo complexation with Fe(0) in syn,exo fashion.[9] In addition, we have previously noted[3] that a lone electron pair on the 7-Lewis base substituent might be capable of entering into an antiaromatic bishomoconjugative electronic interaction with the electrons in the norbornadiene double bond that is syn to that substituent. For the case of, e.g., the reaction of $Fe(CO)_5$ with 7-*tert*-butoxynorbornadiene, the interaction[9a] between the syn,exo (alkene)$Fe(CO)_3$ complex and noncomplexed 7-*tert*-butoxynorbornadiene can be envisioned to occur in the manner shown in Scheme II, thereby affording the observed SXTNS dimer ketone.

The above argument rests upon the assumption that there is sufficient electron density on the 7-Lewis base substituent to render relatively important the interaction of that substituent (i) with Fe(0) in the (alkene)$Fe(CO)_3$ complex and (ii) with the syn double bond in the noncomplexed alkene substrate. Such has been shown to be the case for 7-alkoxynorbornadienes and for *syn*-7-alkoxynorbornenes.[9c] In addition, the results of molecular orbital calculations suggest that the energy of the HOMO of the syn double bond in noncomplexed 7-alkoxynorbornadienes is elevated slightly but significantly relative to that of the norbornadiene double bond that is anti to the 7-substituent, thereby rendering the former to be the more reactive of the two norbornadiene carbon–carbon double bonds in these substrates.[12-14]

The observed lack of regiospecificity in the corresponding iron carbonyl promoted coupling of 7-(benzoyloxy)norbornadiene to carbon monoxide is a mechanistically significant observation that suggests that the electron density on the ether oxygen atom in the 7-benzoyloxy substituent may not be sufficient to direct the course of the $Fe(CO)_5$-promoted coupling reaction exclusively toward the syn double bond in either (or both) the Fe(0)-complexed or the noncomplexed alkene substrate.

An attempt was made to gain direct experimental evidence regarding our hypothesis that electron density on the ether oxygen atom in the 7-benzoyloxy moiety indeed determines the regio- and stereochemistry of coupling of 7-(benzoyloxy)norbornadiene to carbon monoxide. To this end, the thermal reaction of 7-[(*p*-methoxybenzoyl)oxy]-norbornadiene (**6**)[4] with $Fe(CO)_5$ was performed, and the reaction products were isolated and characterized. Here, we sought evidence that back-donation of electron density to the ester carbonyl group by the electron-donating *p*-methoxy substituent might reduce the ability of this carbonyl group to withdraw electron density from the adjacent ether oxygen atom, thereby (i) increasing the electron density on the ether oxygen atom and (ii) possibly rendering this oxygen atom capable of coordination with Fe(0), thereby enabling it to direct coupling to carbon monoxide at the syn,exo double bond in the substrate. Two products were isolated from this reaction: a cage dimer (**7**, 23%)[4] and a dimer ketone (**8**, 4%, Scheme I). The structure of **8** was established via (i) detailed examination of its proton NMR spectrum and (ii) via nuclear magnetic double resonance experiments that are entirely analogous to those described earlier for the case of dimer ketone **4**. As in the case of **4**, the existence of a sharp AB pattern centered at δ 2.5 establishes the trans relationship between the β and β' cyclopentanone carbon–hydrogen bonds. In addition, the existence of stereospecific long-range coupling, ${}^4J_{HH}$,[11] between the vinyl protons (δ 6.18) and the bridge proton C*H*OC(O)Ar (δ 4.85), revealed via nuclear magnetic double resonance experiments, confirms that the bridge 7-(*p*-methoxybenzoyl)oxy substituents occupy anti bridge positions in **8**. Thus, we conclude that **8**, like **4**, possesses the AXTXA configuration. It is clear from this result that the presence of the *p*-methoxy groups in **6** did not significantly affect the course of the Fe(0)-promoted coupling of this substrate to carbon monoxide.[15]

Experimental Section

Melting points are uncorrected. High-resolution mass spectra were obtained by the Midwest Center for Mass Spectrometry at the University of Nebraska—Lincoln.

Reaction of 7-(Benzoyloxy)norbornadiene with $Fe(CO)_5$. To a solution of 7-(benzoyloxy)norbornadiene (10.0 g, 47.1 mmol, prepared by the method of Tanida and Tsuji[16]) in freshly distilled di-*n*-butyl ether (50 mL) under nitrogen was added a solution of $Fe(CO)_5$ (18.5 g, 94.4 mmol) in di-*n*-butyl ether (10 mL). The resulting miture was refluxed with stirring under nitrogen for 72 h and then cooled to room temperature. To the cooled reaction mixture was added a solution of ferric chloride hexahydrate (52 g, excess) in acetone (200 mL), and the resulting mixture was stirred at room temperature for 1 week to decompose unreacted iron pentacarbonyl and any Fe(0) complexes that might be present. Distilled water (300 mL) was then added, and the reaction mixture was extracted with ethyl acetate (7 × 100 mL). The combined extracts were washed with water, dried (anhydrous magnesium sulfate), and filtered. The filtrate was concentrated in vacuo to afford a viscous, dark brown oil. This oil was diluted with an equal volume of absolute ethanol and refrigerated overnight; relatively pure cage dimer **1** (1.5 g, 29%) precipitated under these conditions and could be collected by suction filtration. Pure **1** was obtained via column chromatography on Florisil (100–200 mesh, 10% ethyl acetate–hexane mixed solvent as eluent); a final recrystallization from ethyl acetate–hexane mixed

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[9] (a) Mantzaris, J.; Weissberger, E. *J. Am. Chem. Soc.* **1974**, *96*, 1873; (b) Cf.: Weissberger, E.; Laszlo, P. *Acc. Chem. Res.* **1976**, *9*, 209. (c) Laszlo, P.; Stockis, A. *J. Organomet. Chem.* **1976**, *117*, C41.

[10] *International Tables for X-Ray Crystallography*; Reidel: Dodrecht, Holland, 1983; Vol. 3.

[11] (a) See: Marchand, A. P. *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*; Verlag Chemie International: Deerfield Beach, FL, 1982; pp 174–193. (b) Marchand, A. P.; Rose, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 3724.

[12] Astin, K. B.; Mackenzie, K. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1004.

[13] Mazzocchi, P. H.; Stahly, B.; Dodd, J.; Rondan, N. G.; Domelsmith, L. N.; Rozeboom, M. D.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *92*, 6482.

[14] Marchand, A. P. *Abstracts of Papers*, 38th Southwest and 6th Rocky Mountain Regional Meeting of the American Chemical Society, El Paso, TX, December 1–3, 1982; American Chemical Society: Washington, DC, 1982; Abstract 235.

[15] A referee has suggested that iron coordination instead may occur preferentially to the ester carbonyl oxygen (rather than to the more hindered and less basic ether oxygen) in 7-(benzoyloxy)norbornadiene and in **6**, thereby accounting for the observed lack of stereospecificity in the $Fe(CO)_5$-promoted coupling of these substrates to carbon monoxide. We plan to evaluate this suggestion experimentally in the future.

[16] Tanida, H.; Tsuji, T. *J. Org. Chem.* **1964**, *29*, 849.

solvent afforded pure **1** as a colorless microcrystalline solid, mp 192.5–193.0 °C. Spectral and microanalytical data for **1** have been reported elsewhere.[4]

Isolation of compounds **2**–**5** from the filtrate (after removal of **1** as described above) was accomplished via careful column chromatography on Florisil (100–200 mesh, 15% ethyl acetate–hexane mixed solvent as eluent). The first fraction collected contained unreacted 7-(benzoyloxy)norbornadiene (4.9 g). The second fraction contained a mixture of **3** and **4**. Partial evaporation of solvent from this fraction under ambient conditions resulted in fractional recrystallization. Pure **4** (0.16 g, 3%), mp 252–253 °C, was thereby obtained: IR ($CHCl_3$ solution) 1722 (vs), 1609 (m), 1590 (w), 1495 (w), 1455 (m), 1335 (m), 1319 (m), 1282 (vs), 1189 (m), 1158 (m), 1120 (s), 1074 (m), 1029 (w), 1005 (w), 890 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.32 (AB, $J_{AB} = 8.3$ Hz, 2 H), 2.72 (AB, $J_{AB} = 8.3$ Hz, 2 H), 3.22 (m, 2 H), 2.25 (m, 2 H), 4.89 (t, $J = 1.7$ Hz, 2 H), 6.20 (m, 2 H), 6.22 (m, 2 H), 7.5 (m, 6 H), 8.0 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 45.6 (d), 50.5 (d), 52.8 (d), 57.8 (d), 85.1 (d), 128.4 (d), 129.6 (d), 130.0 (s), 133.1 (d), 133.3 (d), 134.3 (d), 166.8 (s), 217.2 (s); mass spectrum (70 eV), m/e (relative intensity) 452 (molecular ion, 1.0), 105 (100.0), 77 (22.7).

Anal. Calcd for $C_{29}H_{24}O_5$: M_r 452.16237. Found (high-resolution mass spectrometry): M_r 452.16493.

Evaporation of the mother liquor from the second chromatographic fraction resulted in fractional crystallization. Pure **3** (0.11 g, 2%), mp 219–220 °C, was thereby obtained: IR ($CHCl_3$ solution) 2975 (w), 1722 (s), 1605 (m), 1588 (w), 1453 (m), 1355 (w), 1318 (s), 1275 (vs), 1177 (m), 1115 (s), 1088 (s), 1072 (s), 1027 (m), 1003 (m), 910 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.81 (dd, $J_1 = 8.5$ Hz, $J_2 = 3.8$ Hz, 2 H), 2.95 (dd, $J_1 = 8.5$ Hz, $J_2 = 4.8$ Hz, 2 H), 3.22 (m, 2 H), 3.25 (m, 2 H), 4.71 (t, $J = 2.0$ Hz, 2 H), 6.16 (dd, $J_1 = 6.2$ Hz, $J_2 = 3.3$ Hz, 2 H), 6.29 (dd, $J_1 = 6.2$ Hz, $J_2 = 3.3$ Hz, 2 H), 7.42–7.60 (m, 6 H), 7.96 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 41.8 (d), 48.0 (d), 49.2 (d), 58.1 (d), 86.1 (d), 128.5 (d), 129.4 (d), 129.9 (s), 133.2 (d), 134.8 (d), 135.0 (d), 165.6 (s), 223.1 (s); mass spectrum (70 eV), m/e (relative intensity) 452 (molecular ion, 0.1), 105 (100.0), 77 (15.5).

Anal. Calcd for $C_{29}H_{24}O_5$: C, 76.96; H, 5.35. Found: C, 75.32; H, 5.27.

Fractional crystallization of the third chromatography fraction afforded pure **2** (0.05 g, 1%), mp 218.5–219.0 °C: IR ($CHCl_3$ solution) 1719 (s), 1604 (w), 1587 (w), 1452 (w), 1317 (m), 1275 (s), 1115 (s), 1070 (w), 1025 cm^{-1} (w); ^1H NMR (300 MHz, $CDCl_3$) δ 1.97 (ddd, $J_1 = 8.9$ Hz, $J_2 = 2.0$ Hz, $J_3 = 1.0$ Hz, 1 H), 2.03 (dd, $J_1 = 8.9$ Hz, $J_2 = 1.0$ Hz, 1 H), 2.90 (ddd, $J_1 = 8.6$ Hz, $J_2 = 4.4$ Hz, $J_3 = 2.0$ Hz, 1 H), 3.19 (m, 1 H), 3.24 (m, 1 H), 3.42 (dd, $J_1 = 8.6$ Hz, $J_1 = 4.9$ Hz, 1 H), 3.45 (m, 1 H), 3.51 (m, 1 H), 4.84 (t, $J = 1.6$ Hz, 1 H), 4.87 (t, $J = 1.8$ Hz, 1 H), 6.13 (dd, $J_1 = 5.8$ Hz, $J_2 = 2.5$ Hz, 1 H), 6.14 (m, 2 H), 6.19 (dd, $J_1 = 5.8$ Hz, $J_2 = 2.9$ Hz, 1 H), 7.46 (m, 6 H), 7.94 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 41.03 (d), 33.86 (d), 49.37 (d), 50.11 (d), 50.71 (d), 52.64 (d), 56.32 (2C, d), 85.37 (d), 87.78 (d), 128.33 (2 C, d), 129.61 (2C, d), 129.99 (s), 130.04 (s), 131.21 (d), 132.38 (d), 133.04 (d), 133.10 (d), 133.18 (d), 134.26 (d), 166.46 (s), 166.66 (s), 219.09 (s); mass spectrum (70 eV), m/e (relative intensity) 452 (molecular ion, 1.4), 105 (100.0), 77 (14.5).

Anal. Calcd for $C_{29}H_{24}O_5$: C, 76.96; H, 5.35. Found: C, 76.88; H, 5.43.

Fractional recrystallization of the fourth chromatography fraction afforded pure **5** (0.02 g, 0.4%). Subsequent fractions contained 0.67 g of material that was not characterized.

Characterization of **5**: IR ($CHCl_3$ solution) 1710 (s), 1317 (m), 1274 (s), 1213 (m), 1177 (w), 1120 (m), 1109 (m), 1085 (m), 1070 (m), 1027 (m), 1010 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.77–2.80 (m, 4 H), 2.88 (m, 2 H), 3.01 (m, 2 H), 3.02–3.06 (m, 4 H), 5.39 (t, $J = 1.7$ Hz, 2 H), 7.50 (m, 6 H), 7.99 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 41.0 (d), 46.7 (d), 48.0 (d), 49.7 (d), 51.9 (d), 55.1 (d), 83.3 (d), 128.4 (d), 129.6 (d), 129.7 (d), 133.2 (d), 165.7 (s), 219.6 (s); mass spectrum (70 eV), m/e (relative intensity) 452 (molecular ion, 15.3), 105 (100.0), 77 (13.9).

Anal. Calcd for $C_{29}H_{24}O_5$: (M_r + H) 453.1690; Found (high-resolution chemical ionization mass spectrometry): (M_r + H) 453.1685.

Single-Crystal X-ray Structural Analysis of 2. Compound **2** was carefully recrystallized from chloroform–hexane mixed solvent; colorless, irregular crystals were thereby obtained. A fragment of approximate dimensions 0.20 × 0.38 × 0.48 mm was mounted on a Nonius CAD-4 automatic diffractometer equipped with Cu Kα Ni-filtered radiation. A total of 4793 reflections were collected at ambient temperature in the sphere $2° \leq 2\theta \leq 150°$. After averaging, 4668 unique reflections were obtained including 3762 observed reflections where $I_0 \geq 2\sigma(I)$. The triclinic unit cell parameters resulting from least-squares calculations on 25 high 2θ reflections were as follows: $a = 9.198$ (2) Å, $b = 9.968$ (2) Å, $c = 13.054$ (3) Å, $\alpha = 94.23$ (2)°, $\beta = 105.35$ (2)°, $\gamma = 99.77$ (1)°, $V = 1129$ Å^3. The space group[17] $P\bar{1}$ was assumed and gave satisfactory refinement. Other details of data collection were as follows: scan method, $\theta/2\theta$; scan rate, variable up to 45 s per scan; scan range, calculated by 0.90 + 0.20 tan θ, with 25% extension on each side for backgrounds. Three intensity monitors were checked every 2 h of X-ray time and fluctuated randomly 2% over the entire data collection. Three orientation monitors were centered after every 200 observations. With $Z = 2$, the calculated density was 1.331 g·cm^{-3}, and μ(Cu Kα) = 6.47 cm^{-1}. No correction for absorption or secondary extinction was made.

The structure was solved by direct methods calculations.[18] Hydrogen atoms were placed with reference to a difference Fourier map and were refined positionally and isotropically; all non-hydrogen atoms were refined anisotropically. All atoms lie on general positions. Full-matrix least squares on all observed reflections yielded $R = 0.049$ and $R_w = 0.067$.[19] The maximum shift in the last cycle was 0.5σ, the number of variables was 403, and the number of observations was 3762. In a final difference map, the largest peak represented less than 0.2 e Å^{-3}. Neutral atom scattering factors were obtained from ref 20.

Details of the crystallographic experiment are summarized in Table I. The following crystallographic data for **2** are included as supplementary material: (i) atomic positional and thermal parameters for non-hydrogen atoms (Tables A and B, respectively); (ii) bond angles and bond lengths for non-hydrogen atoms (Tables C and D, respectively); (iii) hydrogen atomic parameters (Table E); (iv) least-squares planes (Table F); (v) observed and calculated structure factors (Table G).

Single-Crystal X-ray Structural Analysis of 3. Compound **3** was carefully recrystallized from chloroform–hexane mixed solvent; colorless, flat, fibrous needles were thereby obtained. A single crystal of approximate dimensions 0.15 × 0.48 × 0.60 mm was selected and mounted on a Nonius CAD-4 automatic diffractometer equipped with Mo Kα radiation and a graphite monochrometer. A total of 4084 reflections were collected at ambient temperature in the sphere $3° \leq 2\theta \leq 50°$. After averaging, 3965 unique reflections were obtained including 2165 observed reflections where $I_0 \geq 2\sigma(I)$. The triclinic[21] unit cell parameters resulting from least-squares calculations on 25 high 2θ reflections were as follows: $a = 6.577$ (2) Å, $b = 8.751$ (2) Å, $c = 21.738$ (6) Å, $\alpha = 78.22$ (2)°, $\beta = 81.26$ (3)°, $\gamma = 67.88$ (3)°, $V = 1313$ (14) Å^3. The space group[17] $P\bar{1}$ was assumed and gave satisfactory refinement. Other details of data collection were as follows: scan method, $\theta/2\theta$; scan rate, variable up to 45 s per scan; scan range, calculated by 1.0 + 0.20 tan θ with 25% extension on each side for backgrounds. Three intensity monitors were checked every

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(17) *International Tables for X-Ray Crystallography*, 3rd ed.; Kynoch: Birmingham, England, 1969; Vol. 1.

(18) All computations were performed using local modifications of the programs of SHELX-76: Sheldrick, G. M., University Chemical Laboratory, Cambridge, England, 1986.

(19) $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(20) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

(21) The triclinic cell with $a = 6.577$ Å, $b = 8.751$ Å, $c = 21.738$ Å, $\alpha = 78.22°$, $\beta = 81.26°$, and $\gamma = 67.88°$ can be transformed into a monoclinic C-centered cell by the transformation $|1\,{-2}\,0, -1\,0\,0, 0\,1\,{-1}|$; application of this transformation yields the cell constants $a = 16.214$ Å, $b = 6.577$ Å, $c = 21.713$ Å, $\alpha = 90°$, $\beta = 102.39°$, $\gamma = 90°$. Averaging the observed data as monoclinic resulted in 1992 unique reflections with R(merge) = 0.060. The structure was solved in this setting, space group $C2/c$, and upon convergence afforded final R values of $R = 0.076$ and $R_w = 0.071$ (cf. the final R-values in the triclinic setting, i.e., $R = 0.067$ and $R_w = 0.064$). Hamilton's test of significance[22] was applied to the hypothesis that the monoclinic setting better describes the crystal structure of **3**, with the result that this hypothesis can be rejected at >99% confidence level. Thus, the data reported in Table I for compound **3** are for the molecule in the triclinic setting.

(22) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

2 h of X-ray time and fluctuated randomly 2% over the entire data collection. Three orientation monitors were centered after every 200 observations. With $Z = 2$, the calculated density was 1.329 g·cm^{-3} and (Mo Kα) = 0.52 cm^{-1}. No correction for absorption or secondary extinction was made.

The initial carbon atoms were placed on positions resulting from a direct methods calculation.[18] The complete molecule was located through a series of least-squares and Fourier calculations. Hydrogen atoms were placed in calculated positions and held invariant with U(H) approximately equal to 1.5 times the equivalent isotropic thermal parameter of the carbon atom to which it was bound. All non-hydrogen atoms were refined anisotropically. All atoms lie on general positions. Full-matrix least squares on all observed reflections yielded $R = 0.067$ and $R_w = 0.064$.[19] The maximum shift in the last cycle was $<0.02\sigma$, the number of variables was 307, and the number of observations was 2165. In a final difference map, the largest peak represented <0.20 e Å^{-3}. Neutral atom scattering factors were obtained from ref 20.

Details of the crystallographic experiment are summarized in Table I. The following crystallographic data for **3** are included as supplementary material: (i) atomic positional and thermal parameters for non-hydrogen atoms (Tables H and I, respectively); (ii) bond angles and bond lengths for non-hydrogen atoms (Tables J and K, respectively); (iii) hydrogen atomic parameters (Table L); (iv) least-squares planes (Table M); (v) observed and calculated structure factors (Table N).

Reaction of 7-[(*p*-Methoxybenzoyl)oxy]norbornadiene (6) with Iron Pentacarbonyl. To a solution of **6**[4] (12.37 g, 51.1 mmol) in freshly distilled di-*n*-butyl ether (60 mL) under nitrogen was added a solution of $Fe(CO)_5$ (20.42 g, 104.3 mmol) in di-*n*-butyl ether (15 mL). The resulting mixture was refluxed with stirring under nitrogen for 26 h and then cooled to room temperature. Workup of the reaction mixture was performed by using the procedure described above for the corresponding reaction of 7-(benzoyloxy)norbornadiene with $Fe(CO)_5$. The procedure by which cage dimer **7** was isolated and characterized has been described in an earlier publication along with spectral details and the results of elemental microanalysis of **7**.[4] After removal of **7**, the crude reaction product was further purified via column chromatography on Florisil (100–200 mesh, 15% ethyl acetate–hexane eluent). The first few chromatographic fractions contained unreacted **6**; however, continued elution of the column afforded dimer ketone **8** (0.19 g, 4%). Recrystallization of this material from ethyl acetate–hexane mixed solvent afforded pure **8** as a colorless microcrystalline solid: mp 241.3–241.7 °C; IR (KBr) 1718 (vs), 1609 (s), 1280 (br, s), 1170 (s), 1115 (br, s), 1030 (s), 848 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (*A*B, $J_{AB} = 8.2$ Hz, 2 H), 2.70 (A*B*, $J_{AB} = 8.2$ Hz, 2 H), 3.20 (m, 2 H), 3.32 (m, 2 H), 3.85 (s, 6 H), 4.85 (t, $J = 1.7$ Hz, 2 H), 6.18 (m, 2 H), 6.21 (m, 2 H), 6.87 (*A*B, $J_{AB} = 8.9$ Hz, 4 H), 7.89 (A*B*, $J_{AB} = 8.9$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 45.57 (d), 50.53 (d), 52.84 (d), 55.36 (d), 57.87 (d), 84.90 (d), 113.61 (d), 122.39 (s), 131.66 (d), 133.23 (d), 134.29 (d), 163.53 (s), 166.49 (s), 216.84 (s); mass spectrum (70 eV), *m/e* (relative intensity) 512 (M$^+$, 1.0), 136 (9.7), 134 (100.0), 77 (6.1).

Anal. Calcd for $C_{31}H_{28}O_7$: C, 72.64; H, 5.51. Found: C, 72.35; H, 5.44.

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Registry No. 1, 89278-39-7; 2, 104351-88-4; 3, 104419-67-2; 4, 104419-68-3; 5, 104351-89-5; 6 (Ar = Ph), 4796-68-3; 6 (Ar = *p*-$MeOC_6H_4$), 7109-81-1; 7, 89321-10-8; 8, 104351-90-8; $Fe(CO)_5$, 13463-40-6.

Supplementary Material Available: Molecular drawings of **2** and **3** (Figures 1 and 2, respectively). Tables of (i) atomic positional and thermal parameters for carbon, hydrogen, and oxygen, (ii) bond angles, (iii) bond lengths, (iv) hydrogen parameters, and (v) least-squares planes, for **2** and **3** (18 pages); (vi) observed and calculated structure factors for **2** and **3** (40 pages). Ordering information is given on any current masthead page.

Concerning the Hammett Acidity Function Method for Determination of pK_a Values

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Physicochemical relationships incorporating pK_a values derived from the Hammett acidity function method (HAFM), on the one hand, and the Cox–Yates excess acidity function method (EAM), on the other, are compared. To the extent that one accords authenticity to such relationships, the estimates of pK_a values derived from HAFM may approximate, in some cases, more nearly to the correct thermodynamic quantities than those derived from EAM.

Introduction

Within the relatively narrow range of pH of approximately 2–12, where aqueous solutions may be considered ideal, the procedure for measurement of accurate pK_a values is straightforward. Outside this range, where activity can no longer be equated to concentration, the theory to be employed becomes more imprecise and ambiguous, and currently presents some confusion. This is a very undesirable situation, however, because the property of acidity of organic molecules is a fundamentally important one. Chemists in general thus require an authenticated, agreed, and standard procedure for obtaining estimates of pK_a values on which some reliance can be placed.

Two main procedures may be discerned: the Hammett acidity function and the excess acidity function approaches. It is the purpose of this paper to attempt an objective appraisal of these methods and to discuss which one yields pK_a estimates most nearly relating to ideal conditions. It may be noted that investigators in this area are particularly well served by reviews, which give good accounts of the state of play in both acid and basic media, at the time of their production. These culminate most

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