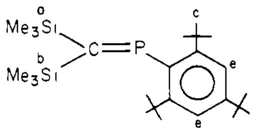
calcd, 538.3164; found, 538.3172. On the basis of ^{31}P NMR spectroscopy, the yields of **1**–**3** were 20%, 60%, and 20%, respectively. The 81.03-MHz $^{31}P\{^{1}H\}$ NMR spectrum of **3** consists of an AB pattern with δ_A +533.1,[5] δ_B +530, and J_{PP} = 619.7 Hz. For single-bonded trivalent phosphorus compounds, J_{PP} falls in the range 200–300 Hz.[6] We attribute the significantly larger magnitude of J_{PP} in **3** to shortening of the phosphorus–phosphorus bond length and to π-bond formation rather than to changes in P(3s) character because the P–P–C bond angle in **2** is approximately the same as that in the diphosphines $(Mes)_4P_2$[7] and $(Cy)_4P_2$)[8] (Mes = mesityl, Cy = cyclohexyl). The ^{31}P chemical shift of **3** is also of interest. While the average chemical shift of **3** (+531.5 ppm) falls between those of the symmetrically substituted diphosphenes **1** (+599.6 ppm) and **2** (+494.0 ppm), the chemical shift difference between the A and B nuclei in **3** is only 3 ppm, thus suggesting extensive charge delocalization in the phosphorus–phosphorus double bond. Unlike the symmetrical diphosphenes **1** and **2**, which exhibit "deceptively simple" triplet $^{13}C\{^{1}H\}$ patterns for the ortho (2,4,6-$(t\text{-Bu})_3C_6H_2$) and $(Me_3Si)_3C$ carbons,[4b] the corresponding resonances for unsymmetrical phosphene **3** comprise doublets of doublets. $^{13}C\{^{1}H\}$ NMR (22.615 MHz, Me_4Si) for **3**: δ 33.9 ($o\text{-}Me_3$C, dd, J_{PCCCC} = 5.5, J_{PPCCCC} ~ 1.0 Hz), 35.5 ($(Me_3Si)_3C$, dd, J_{PC} = 116.2, J_{PPC} = 11.8 Hz), 4.5 ($(Me_3Si)_3C$, dd, j_{PCSiC} = 4.3, J_{PPCSiC} ~ 1.0 Hz). The four-bond coupling between P and the Me carbons of the ortho-t-Bu groups is quite large (5.5 Hz) and suggestive of a through-space interaction. Compound **3** is not as stable as its symmetrical counterparts **1** and **2**, undergoing decomposition in ~2 days at ambient temperature to produce (2,4,6-$(t\text{-Bu})_3C_6H_2$)PH_2 as the major product.

Since we have shown[4b] that **1** can be prepared in high yield by treating $(Me_3Si)_3CPCl_2$ with $(Me_3Si)_3CLi$, we examined the reaction of this lithium reagent with $(Me_3Si)_3CPCl_2$/(2,4,6-$(t\text{-Bu})_3C_6H_2$)PCl_2 mixtures in THF solution. This reaction produced small quantities of **1** and **2**; however, the major product exhibited a ^{31}P NMR singlet at 393 ppm. Identification of this material as the new phosphaalkene **4** is based on its independent synthesis



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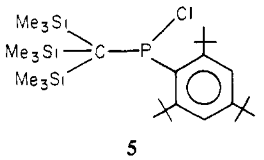
by the following two-step procedure: (i) dehydrochlorination of $(Me_3Si)_2CHPCl_2$ with 1,4-diazabicyclo[2.2.2]octane (Dabco) to form $(Me_3Si)_2C{=}PCl$;[9] (ii) treatment of $(Me_3Si)_2C{=}PCl$ with 2,4,6-$(t\text{-Bu})_2C_6H_2Li$ in hexane/THF solution. **4**: HRMS calcd 434.2953, found 434.2961; ^{1}H NMR (90 MHz) δ 0.2 (Me_3Si(a), d, 9 H, J_{PCSiCH} = 1.5 Hz), –0.4 (Me_3Si(b), s, 9 H), 1.45 (t-Bu(c), s, 18 H), 1.25 (t-Bu(d), s, 9 H), 7.35 (CH(e), s, 2 H). Compound **4** is the exclusive product of the reaction of (2,4,6-$(t\text{-Bu})_3C_6H_2$)PCl_2 with $(Me_3Si)_3CLi$, a process that proceeds presumably via Me_3SiCl elimination from **5**. Finally, it is of interest



5

to note that the reaction of $(Me_3Si)_3CPCl_2$ with $(Me_3Si)_3CLi$ does not result in detectable quantities of the phosphaalkene $(Me_3Si)_2C{=}PC(SiMe_3)_3$ (**6**).[10]

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-8205871) and the Robert A. Welch Foundation for generous financial support.

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(5) Positive ^{31}P chemical shifts are downfield form external 85% H_3PO_4 and vice versa.

(6) Harris, R. K.; Norval, E. M.; Fild, M. *J. Chem. Soc., Dalton Trans.* **1979**, 826–831.

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(8) Richter, R.; Kaiser, J.; Sieler, J.; Hartung, H.; Peter, C. *Acta Crystalogr., Sect. B* **1977**, *B33*, 1887–1892.

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(10) We have prepared phosphaalkene **6** via the reaction of $(Me_3Si)_2C{=}PCl$ with $(Me_3Si)_3CLi$; HRMS calcd 420.2104, found 420.2117; $^{31}P\{^{1}H\}$ NMR (36.43 MHz) δ 422 (s).

Toward Tricyclo[2.2.2.2]decane. 1. [*n*.2.2.2]Paddlane Systems, *n* = 10–14

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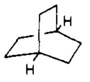
Received December 17, 1982

Consider bicyclo[2.2.2]octane (**1**). The molecule is stable and only slightly strained. The same would be true were the bridgehead hydrogens of **1** replaced by a long enough chain of *n* methylene groups (**2**, the [*n*.2.2.2]paddlanes[1]). Were *n* made smaller, the strain would increase; the geometry about the bridgehead atoms would certainly change. At the symmetrical extreme, when *n* is 2, there would probably be a coplanar (**3a**) or pyramidal (**3b**) arrangement of substituents about these bridgeheads.[2] The associated strain energy is then calculated to be well above 300 kcal/mol.[2b] Thus, between *n* is large and *n* is small the bridgehead atoms of the [*n*.2.2.2]paddlanes must undergo gross rehybridization. We have set out to explore this systematically.[3] Here we report our first finds.



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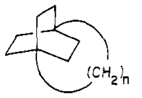

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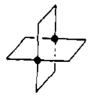
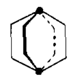
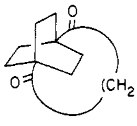


3a



3b

Reaction of bicyclo[2.2.2]octane-1,4-dialdehyde[4] with lithium metal and 1,12-dibromododecane under specially developed conditions[4] gave [14.2.2.2]paddlanedione **4**, mp 98–99 °C, and the "double" paddlane **5**, mp 125–126 °C. Although the yield of paddlane **4** is not good (15%), the starting materials are readily available, and it is easy enough to accumulate substantial quantities of the compound.



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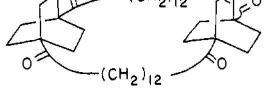

5

The [14.2.2.2]paddlane **4** is the first of this dimension with all ethano bridges unsubstituted. Its ^{1}H NMR spectrum (Figure 1a) is interesting; the 12 protons on the three ethano bridges appear magnetically equivalent at 1.83 ppm even at 500 MHz. Thus, on this NMR time scale, their environment is being averaged by rotation of the bicyclooctane subunit through the large loop of the fourth paddlane bridge. Molecular mechanics calculations (MM2)[5] indicate that this bridging of the 1,4-bicyclooctane

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(1) This nomenclature is due to J. J. Bloomfield: Hahn, E. H.; Bohm, H.; Ginsburg, D. *Tetrahedron Lett.* **1973**, 507.

(2) (a) See the discussion in the following: Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; Chapter 6. (b) Würthwien, E.-U.; Chandrasekhar, J.; Jemmis, E. D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1981**, *22*, 843. (c) Wiberg, K. B.; O'Donnell, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 6660.

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(4) See Supplementary material.

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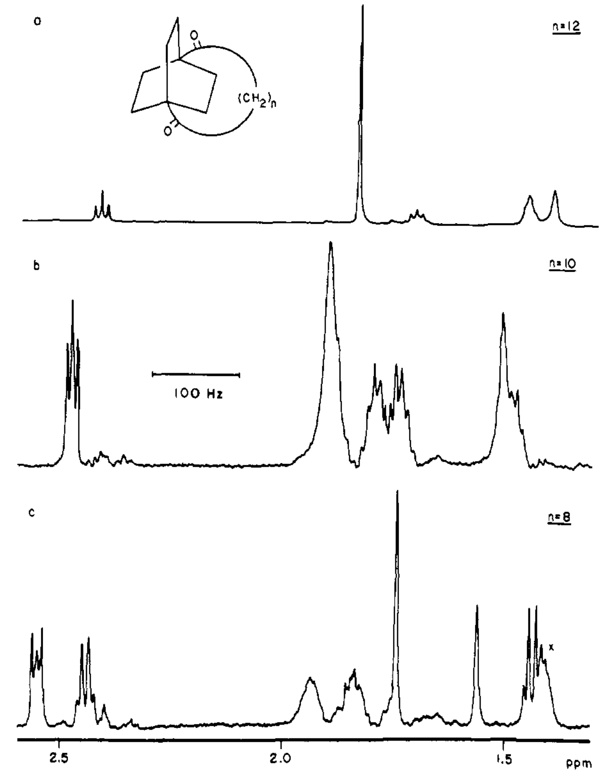


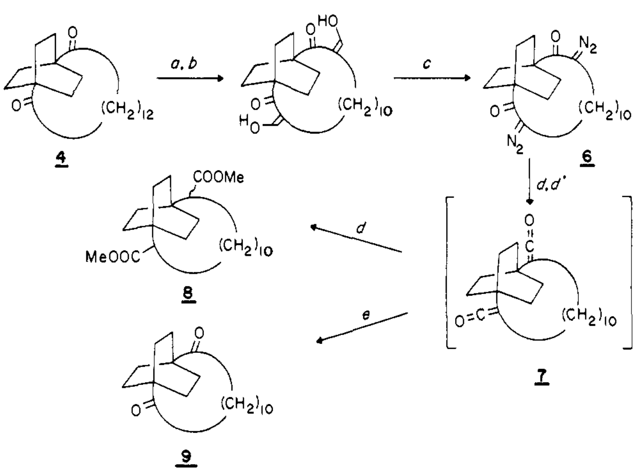
Figure 1. 500-MHz ^{1}H NMR spectra of paddlanes **4** (a), **9** (b), **10** (c) in CDCl$_3$ at ambient temperature.

positions engenders less than a few degrees distortion from the C_3 axis of bicyclo[2.2.2]octane. It is possible, however, to detect chemically conformational constraints on the large ring. Treatment of the bis(tosylhydrazone) of **4** with methyl lithium gave the 2,14-diene in excellent yield, but only the isomer cis at both double bonds; mp 84.5–85.2 °C; ^{1}H NMR (500 MHz) δ 5.35 (2 H, dt, J = 12, 9 Hz), 5.20 (2 H, d, J = 12 Hz). Less than 2% of other geometric isomers was found. Such reactions on medium-to-large ring monocycles give olefin mixtures.[6] Although these eliminations are not thermodynamically controlled, it is clear that the difficulty (~8 kcal/mol) engendered in bridging the 1,4-positions of a bicyclooctane nucleus with a chain containing the "misdirection" of a trans-olefin unit is being felt.

Lower [*n*.2.2.2]paddlanes were reached by Wolff ring contractions. The bis(diazo ketone) **6** was made from **4** as shown in Chart I.[4] Ultraviolet irradiation of **6** in methanol solution gave a mixture (meso, *dl*) of the [12.2.2.2]paddlane diesters **8** via the bis ketene **7**. More pertinent to our purpose here, irradiation of **6** in methylene chloride at −70 °C (**6** → **7**) followed by reaction at −70 °C with ozone in the presence of propionaldehyde[9] allowed direct preparation of the [12.2.2.2]paddlanedione **9**.

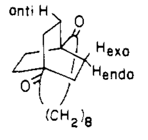
The 500-MHz ^{1}H NMR spectrum of **9** is reproduced in Figure 1b. The point of interest is the resonance at δ 1.89, assignable to the 12 protons on the ethano bridges of the bicyclooctane unit. Its width at halfheight is approximately 18 Hz, over 10 times that of the corresponding resonance in the higher paddlane **4**. Clearly, the contracted ring is interfering with the time-averaging process of rotation of the bicyclooctane unit. As expected, observation of this phenomenon is temperature and field dependent; at 270 MHz and 19 °C the resonance has a width at half-height of about 10 Hz; at 56 °C and the same field, $W_{h/2}$ is ca. 2 Hz.

Chart I



[a] (CH$_2$OH)$_2$, *p*-TsOH, benzene reflux. [b] POCl$_3$/DMF, trichloroethylene, 70 °C, 20 h.[7] [c] TsN$_3$, Et$_3$N, CH$_2$Cl$_2$, 0 °C, 2 h and then −20 °C, 48 h.[8] [d] $h\nu$ (Hanovia 450 W, Pyrex), CH$_3$OH, −70 °C, 15 min. [d'] Same but CH$_2$Cl$_2$. [e] O$_3$, CH$_3$CH$_2$CHO, −70 °C.

Repetition of the sequence in Chart I, but now starting with paddlane **9**, gave the [10.2.2.2]paddlane **10**, the smallest [*n*.2.2.2]paddlane characterized to date. Its 500-MHz ^{1}H NMR spectrum, reproduced in Figure 1c, is totally different from those of the larger paddlanes. The protons on the bicyclooctane subunit are no longer made magnetically equivalent. Instead, there are resonances for three different types of protons on the bicyclooctane frame, corresponding to expectation if its rotation is frozen out on the NMR time scale.[10] Of these three signals, that at lowest field (2.43 ppm) is assigned H$_{\text{endo}}$ on the idea that steric compression against the methylenes of the large bridge causes the downward shift. Complementally, H$_{\text{exo}}$, its geminal mate, is shifted upfield (1.41 ppm). Double-resonance experiments confirm their strong spin coupling. The resonance of 1.73 ppm is assigned to the four equivalent hydrogens on the ethano bridge anti to the locked-in long loop. This signal is fairly sharp, broadened only by small W coupling to H$_{\text{endo}}$; it is narrowed when the H$_{\text{endo}}$ resonance is irradiated.[11]



10

Paddlanedione **10** is the lowest member of the homologous set that can be constructed with rigid, space-filling models. The fit of ethano bridges into the cavity of the large bridge is exceptionally tight, and there is little conformational flexibility. MM2 calculations indicate that the "pull" of the loop on the external bridgehead bonds of the bicyclooctane is becoming significant. The bonds are fully 11° off the C_3 axis of an unconstrained bicyclooctane. Further shortening of the loop, a process now in progress, should increase this dramatically and begin to reveal

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(5) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. The program used was written and parametized by N. L. Allinger and Y. H. Yuh (University of Georgia, Athens, GA, 1980). A copy was obtained from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana (QCPE 395).

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(10) Cf.: Wynberg, H.; Helder, R. *Tetrahedron Lett.* **1973**, 4321.

(11) Note the arithematical average of the three resonances seen for the bicyclooctane protons in **10** is essentially equal to the environmental average seen in the ^{1}H NMR spectra of **4** and **9**. Contractions of monodiazo ketones produced incidentally from diones **4** and **9** gave the [13.2.2.2]- and [11.2.2.2]paddlanediones, respectively. The ^{1}H NMR of the former is very like that of **4**; the latter, like that of **10**.

the nature of the rehybridization of the bridgehead atoms.

Acknowledgment. This research was supported by the National Science Foundation (CHE-8118391) and the National Institutes of Health (GM 29258-10).

Supplementary Material Available: Preparation of bicyclo[2.2.2]octane-1,4-dialdehyde, experimental details for **4**, and characterization of important intermediates (1 page). Ordering information is given on any current masthead page.

Photoreduction of Keto Carboxylic Acid Derivatives to Oxyacid Derivatives Catalyzed by ZnTPPS-Quinolinium-3-carboxamide-CTAB Micelle

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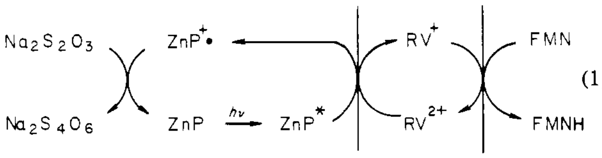
Received December 22, 1982

Reduction of keto carboxylates or other carbonyl compounds via biomimetic or synthetic organic approaches has been the subject of many investigations.[1] Especially important is the reduction of carbonyl compounds in an *aqueous solution* "induced" by an electron-transport species such as NAD or certain artificial NAD equivalents, in consideration that the enzymatic reductions are carried out in an aqueous solution mediated by NAD(P) in the presence of a dehydrogenase.[2] However, the reductions under such conditions have seldom been successful by the use of an artificial NAD equivalent, due to problems of either (1) undesirable side reactions[3] and/or (2) insufficient reactivity[1] of NADH or its artificial equivalent under the conditions.[4] In the present paper we report that efficient endoergonic reduction of benzoylformic acid derivatives takes place photochemically with $Na_2S_2O_3$ in the presence of a specifically functionalized micelle.

Very efficient charge separation can be achieved in two-phase systems[5] or multiphase systems. Further extension of the successful charge separation to the efficient electron fixation at the reduction end leads to the FMNH production via an artificial photosynthesis of bacteria type (see eq 1).



(1)

Thus, a micellar system consisting of ZnTPPS (ZnTPP *p*-tetrasulfonate, 2 × 10^{-6} M) as a photocatalyst, quinolinium-3-carboxamide (**2**) (7 × 10^{-5} M) as an electron acceptor, $Na_2S_2O_3$ (0.02 M) as an electron source, and CTAB (5 × 10^{-3} M) was prepared and degassed under vacuum followed by Ar substitution. The aqueous micellar solution was irradiated by a 500-W tungsten lamp (>370 nm, with a Toshiba UV-37 filter, with water cooling).

Table I. Recycling of Photocatalyst[a]

substrate	$PhCOCO_2Me$	$PhCH_2$-$COCO_2Me$	isatin
ZnTPPS, M	1.1 × 10^{-6}	1.8 × 10^{-6}	5.1 × 10^{-5}
obsd recycling[d]	82	60[d]	2.1
theor recycling[c]	330	64	30

[a] Substrate = 1.4 × 10^{-3} M, $[ZnTPPS]_0$ = 2.9 × 10^{-6}, $[\mathbf{2a}]_0$ = 2.1 × 10^{-5} M, $[Na_2S_2O_3]_0$ = 0.18 M, CTAB, 0.12 M, *hν* (>370 nm). [b] Electron utilized for reduction/ZnTPPS used. [c] Based on ZnTPPS consumed. [d] Recovery of the starting keto carboxylate was poor.

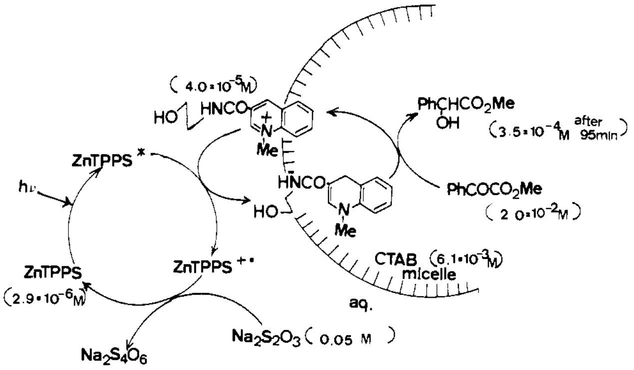
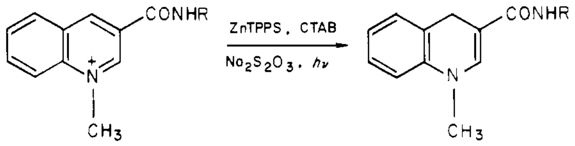


Figure 1. Benzoylformate photoreducing micelle.

After 10 min of irradiation practically quantitative conversion of **2** to the corresponding dihydro derivative, **3**, was observed (eq 2).



(2)

2a, R = CH_2CH_2OH
b, R = H

3

In an interesting contrast, no detectable amount of **3** was formed from the irradiation of the homogeneous solution of **2** under the corresponding conditions (without CTAB). Therefore, it is evident that phase transfer of **3** from an aqueous to a hydrophobic region is necessary and important for the effective production of the NADH equivalent. The following observations are noteworthy: (a) a recycling number of the photocatalyst (reduction equivalent/catalyst used) was found to be ca. 70; (b) no appreciable decomposition of the photocatalyst was observed; (c) the present reduction is an energetically uphill conversion by 15–18 kcal/mol, and reduction of **2** to **3** with $Na_2S_2O_3$ does not occur without irradiation.

The presently prepared dihydroquinoline **3a** incorporated in the photosynthesizing micelle was used for the reduction of benzoylformates. Thus, methyl benzoylformate was reduced to the corresponding mandelate in a good yield (eq 3 and Table I) and

$$PhCOCO_2Me + \mathbf{3a} \rightarrow PhCHOHCO_2Me + \mathbf{2a} \quad (3)$$

with a reasonable rate. However, dihyroquinoline **3b**, having no substituent on the amide nitrogen, showed only slow rate and very poor yield of mandelate.

On the basis of these observations, full construction of a "keto carboxylate photoreducing micelle" was successfully made as shown in Figure 1. Recycling numbers of the photocatalyst and the electron-transport catalyst were excellent, and a remarkable amount of methyl mandelate was accumulated in the micelle as shown in Figure 1. The methyl mandelate formed was extracted with ether (3 × 2 mL) from the aqueous solution, analyzed by HPLC, and purified. Interestingly, under the conditions, the observed steady-state concentration of **3a** was low, suggesting that the reduction of the benzoylformate with **3a** in the micelle was quite fast. Other keto carboxylic acid derivatives were similarly reduced with $Na_2S_2O_3$ by the present "photoreducing micelle".

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