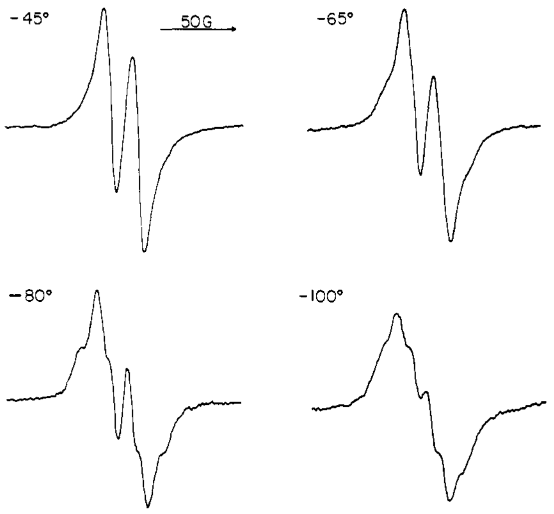

Figure 2. ESR spectra at four different temperatures of 92% ^{13}C-enriched $HFe_3(CO)_{11}\cdot$ in THF.

definitely at this temperature but decays rapidly above −40 °C. Its ESR spectrum is a doublet (18.4 G) with a line width of 5 G and a g factor of 2.0635.[10] This species can also be obtained starting from 92% ^{13}C-enriched $Fe(CO)_5$ as mentioned in the preceding communication (cf. ref 8).[11] At −45 °C the presence of ^{13}C atoms merely broadens the line width. On lowering the temperature, however, the reversible spectral changes shown in Figure 2 are observed which are clearly caused by the slowing down of a rapid exchange of ^{13}CO ligands between different sites. No further changes occur below −100 °C, indicating that the cluster is now static on the ESR time scale. Although the resolution is wanting, the spectrum at −100 °C clearly consists of six lines. It follows that each line of the original and invariant doublet is now split into a triplet with a splitting of ~6 G. Thus, the static $HFe_3(CO)_{11}\cdot$ species has a set of *two equivalent carbonyls* which interact appreciably with the unpaired electron. Interestingly, the diamagnetic analogue $HIII^-$ is also a highly fluxional molecule[12] whose slow-exchange ^{13}C NMR spectrum is consistent with its structure in the solid state.[13] The latter is related to that of HII^-, shown above, by the replacement of one of the bridging carbonyls with an octahedral $Fe(CO)_4$ group. The presence of two equivalent CO's in $HIII\cdot$ does not exclude an isostructural relationship with $HIII^-$ which has five equivalent pairs of CO's.[14]

Yet another very unstable paramagnetic hydride was observed in the low-temperature oxidations with $AgBF_4$ of THF solutions of II^- to which an equivalent of $HBF_4{\cdot}Et_2O$ had been added. The spectrum of this species at −80 °C is a doublet of 23.9 G with a line width of ~5 G and a g factor of 2.0276. It is assigned provisionally to the paramagnetic hydride $HFe_4(CO)_{13}\cdot$.[15]

Acknowledgment. I am very grateful to B. F. Gordon and D. J. Jones for technical assistance, Professor D. F. Shriver for a sample of $[PPN][HFe_3(CO)_{11}]$ and useful comments, Professor J. San Filippo, Jr., and Dr. D. L. Thorn for informative discussions, Professor B. Hutchinson for a sample of $^{57}Fe(CO)_5$, and Dr. William J. Cote for the synthesis of $H_2Fe(CO)_4$.

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[10] Expectedly, the deuterated analogue, $DFe_3(CO)_{11}\cdot$, gave a single line ~10 G wide.

[11] In the same manner we have also obtained $HFe_3(CO)_{11}\cdot$ from $^{57}Fe(CO)_5$. Unfortunately, the ^{57}Fe hyperfine structure cannot be resolved, and the lines of the H doublet are simply broadened ($\Delta H \sim 7.2$ G).

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[14] We again suppose (cf. ref 9) that the strongly interacting pair of CO's is the terminal pair trans to the bridging H atom.

[15] **Note Added** in Proof: Similar oxidations of $[PPN][HFe_4(CO)_{13}]$ failed so far to confirm this assignment perhaps because of the thermal instability of the paramagnetic hydride. I thank Professor D. F. Shriver and Dr. K. Whitmire for samples of $[PPN][HFe_4(CO)_{13}]$.

A Systematically Designed Homogeneous Oscillating Reaction: The Arsenite-Iodate-Chlorite System

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The number of homogeneous chemical reactions known to exhibit sustained oscillations[1] is relatively small,[2] and all those reported thus far have either been discovered serendipitously or are variants or combinations of previously known oscillators.[3] The recent surge of interest and progress in understanding the nature of chemical oscillation suggests that (a) the discovery of more fundamentally different oscillating reactions would be of major significance as a testing ground for general theories of dynamical behavior and (b) the time may be at hand when the criteria for oscillation are well enough understood to provide practical guidelines for the design of new oscillators. In this communication we present what we believe to be the first report of a systematically designed homogeneous oscillating reaction—the arsenite–iodate–chlorite system.

Although no necessary and sufficient set of conditions for chemical oscillation is known, several factors which enhance the likelihood of oscillation are clear. Maintenance of the system far from equilibrium is essential for sustained oscillations. Secondly, although it is not absolutely required if sufficiently complex feedback loops (e.g., cross-catalysis, autoinhibition) are present, autocatalysis is found in nearly all known chemical oscillators. Finally, it has been suggested[4] that many systems which exhibit bistability should be capable of oscillation when subjected to an appropriate feedback.

In order to maintain our system far from equilibrium, we have carried out our experiments in a continuous flow stirred tank reactor (CSTR). We set out to choose an autocatalytic reaction which could give rise to two stable steady states under the same set of external constraints. For the autocatalytic system, we chose the arsenite–iodate reaction (eq 1), which is autocatalytic in

$$3H_3AsO_3 + IO_3^- \rightarrow 3H_3AsO_4 + I^- \qquad (1)$$

iodide.[5] A study of this reaction in the CSTR[6] showed that it is indeed bistable over a wide range of flow rates and inlet concentrations.

For oscillation production, the feedback reaction to be coupled to a bistable system need only produce an appropriate change in the region of stability of the steady states.[4] However, iodide, the autocatalytic species in reaction 1, is also known to react with chlorite in reaction 2, which is autocatalytic in iodine.[7] We

$$4H^+ + ClO_2^- + 4I^- \rightarrow 2H_2O + Cl^- + 2I_2 \qquad (2)$$

therefore chose to introduce chlorite into our system in an attempt to induce oscillation.

Figure 1 shows the spectrophotometric absorption at 460 nm, where both I_3^- and I_2 absorb significantly, and the potential of an iodide-sensitive electrode in the CSTR as a function of time. With a residence time of 400 s at 25 °C and pH 2.35, oscillations, with periods between 15 s and 4 min, are observed over a range of $[KIO_3]_0$ from 24×10^{-3} to 80×10^{-3} M, $[As_2O_3]_0$ from 1.5×10^{-3} to 6×10^{-3} M, and $[NaClO_2]_0$ from 1.5×10^{-3} to 6×10^{-3} M. Note that the iodide concentration varies by a factor of more than 10^5 during each oscillation.

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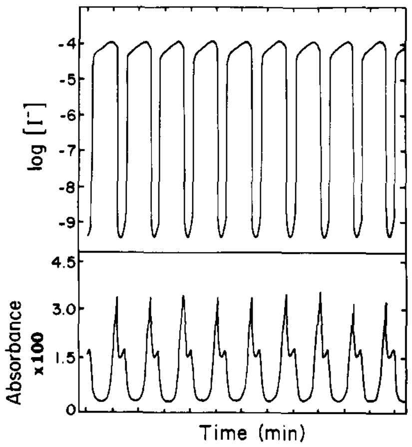

Figure 1. Oscillations of the iodide concentration and absorption per cm path length at 460 nm for $[KIO_3]_0 = 24 \times 10^{-3}$ M, $[As_2O_3]_0 = 2 \times 10^{-3}$ M, $[NaClO_2]_0 = 2 \times 10^{-3}$ M with $[Na_2SO_4]_0 = 0.1$ M, $[H_2SO_4]_0 = 0.01$ M, residence time = 400 s and $T = 25$ °C. Concentrations are given in the reactor after mixing but before any reaction takes place.

In some regions of the phase diagram, one or more stable steady states may coexist with the oscillatory state. Because of this complication, it is most convenient to initiate the oscillations by a single addition of 10^{-3} M iodide to the reactor.

In future papers we shall present further experimental data as well as a discussion of the mechanism of the oscillating arsenite–iodate–chlorite system. Detailed treatments of the mechanism of the arsenite–iodate bistability and of the chlorite–iodide system in a CSTR will also appear elsewhere.

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Pentaprismane[1]

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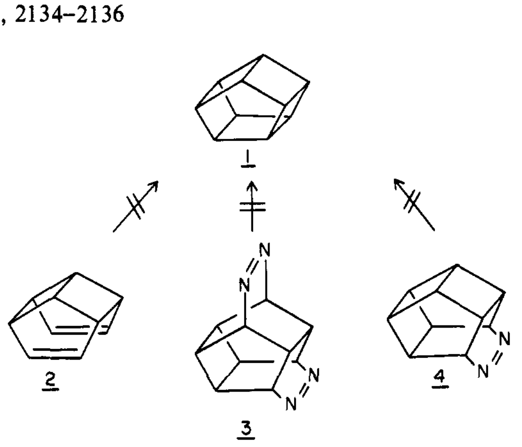
Pentaprismane (**1**) is composed of ten identical methine units arranged at the corners of a regular pentagonal prism (D_{5h} symmetry) and bound into two parallel 5-membered rings conjoined by five 4-membered rings. Empirical force-field calculations put the total strain energy at 135–145 kcal/mol.[2] Many efforts to construct this ring system have failed. Hypostrophene (**2**), an attractive and seemingly appropriate precursor, has been prepared in this laboratory and independently in those of Paquette and Pettit, but no one has been able to effect the called-for photoclosure to pentaprismane.[3] Synthesis by photo/thermal extrusion of molecular nitrogen from diaza compounds **3** and **4** has been attempted by Shen and by Allred, respectively, but again without success.[4] Various rationalizations for these failures have been put forth;[4,5] suffice it to say here, pentaprismane has been recognized for its "extraordinary synthetic inaccessibility".[4b] We report now the first synthesis of pentaprismane; the route starts with a new synthesis of homopentaprismanone and proceeds by bridgehead functionalization of this cage compound and ultimate ring contraction.


1
2
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Homopentaprismanone (**12**) was first prepared by Pettit and co-workers in 1971 starting with photoaddition of cyclobutadiene iron tricarbonyl to tropone ketal.[6] Although conceptually fascinating, the approach is useless synthetically; the starting materials are difficult to obtain, and the ultimate yield of homopentaprismanone is very low. Taking cues from our own and the various other published preparations of homohypostrophene and homopentaprismane,[7] we have developed a new approach to this ketone (Scheme I). The overall yield is now reasonable (34%), and as the starting material is easily made by Diels–Alder reaction of readily available addends,[8] substantial amounts of homopentaprismanone can be accumulated without difficulty.

Favorskii contractions (semibenzilic rearrangements) have been uniquely successful for the synthesis of strained polycyclic compounds related to cubane.[9] The reaction as usually done requires an α-haloketone. An early idea in our planning for pentaprismane was to take compound **6** through Scheme I without the dechlorination step. This might have given tetrachlorohomopentaprismanone, seemingly ready for contraction to the prismane.[9b–e] However, on reflection, it seemed likely that the chlorine substituents would not be passive through the sequence. Further, it is known that Haller–Bauer cleavage of nonenolizable ketones, the competing reaction in Favorskii contractions,[9b,d] is favored by such electronegative, anion-stabilizing groups. Thus, the decision was made to remove the chlorines at the beginning of the scheme and, consequently, to develop methodology to introduce the necessary leaving group directly onto homopentaprismanone.

Functionalization of homopentaprismanone α to the carbonyl groups involves invasion at the bridgehead, a serious problem in such rigid systems. We speculate that the best way will in time turn out to be via the bridgehead anion, taking advantage of inductive stabilization by the carbonyl group. The technology for doing this has yet to be found. Perforce, we developed the quite different approach shown in Scheme II. This cleavage-recoupling procedure should be applicable to α functionalization of other 7-norbornanones as well. For the case at hand, the yield averages 40–45% overall. There is little problem preparing several

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(1) Hexacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,9}.0^{5,8}]decane.

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